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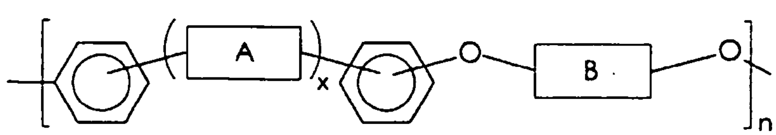
(71) Applicant: XEROX CORPORATION
Rochester New York 14644 (US)

(72) Inventors:
- Fuller, Timothy J.
  Pittsford, NY 14534-4023 (US)
- Narang, Ram S.
  Fairport, NY 14450 (US)
- Smith, Thomas W.
  Penfield, NY 14526 (US)
- Luca, David J.
  Rochester, NY 14609 (US)
- Crandall, Raymond K.
  Pittsford, NY 14534 (US)

(74) Representative: Pike, Christopher Gerard et al
Rank Xerox Ltd.,
Patent Department,
Parkway
Marlow, Buckinghamshire SL7 1YL (GB)

(54) **Process for haloalkylation of high performance polymers**

(57) Disclosed is a process which comprises reacting a polymer of the general formula



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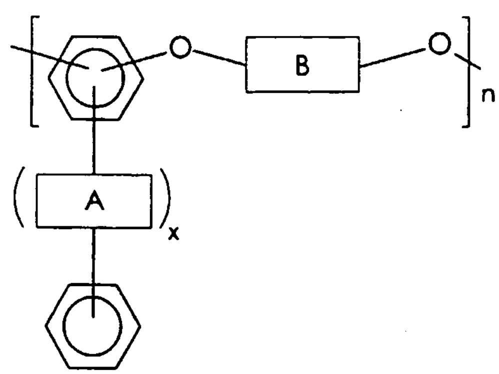

wherein x is an integer of 0 or 1, A and B are specified groups, and n is an integer representing the number of repeating monomer units, with an acetyl halide and dimethoxymethane in the presence of a halogen-containing Lewis acid catalyst and methanol, thereby forming a haloalkylated polymer. In a specific embodiment, the haloalkylated polymer is then reacted further to replace at least some of the haloalkyl groups with photosensitivity-imparting groups. Also dis-

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closed is a process for preparing a thermal ink jet printhead with the aforementioned polymer.

Description

The present invention is directed to a process for preparing haloalkylated high performance polymers and to methods for making photoresists with curable derivatives of these polymers. The present invention is also directed to processes for preparing improved photoresist compositions and improved thermal ink jet printheads with these polymers.

In microelectronics applications, there is a great need for low dielectric constant, high glass transition temperature, thermally stable, photopatternable polymers for use as interlayer dielectric layers and as passivation layers which protect microelectronic circuitry. Poly(imides) are widely used to satisfy these needs; these materials, however, have disadvantageous characteristics such as relatively high water sorption and hydrolytic instability. There is thus a need for high performance polymers which can be effectively photopatterned and developed at high resolution.

One particular application for such materials is the fabrication of ink jet printheads.

Other microelectronics applications include printed circuit boards, lithographic printing processes, and interlayer dielectrics.

Copending application U.S. Serial No. 08/705,375 discloses an improved composition comprising a defined photopatternable polymer containing at least some monomer repeat units with photosensitivity-imparting substituents.

Copending application U.S. Serial No. 08/705,365 discloses a composition which comprises (a) a defined polymer containing at least some monomer repeat units with photosensitivity-imparting substituents which enable crosslinking or chain extension of the polymer upon exposure to actinic radiation; (b) at least one member selected from the group consisting of photoinitiators and sensitizers; and (c) an optional solvent.

Copending application U.S. Serial No. 08/705,488 discloses a composition comprising a polymer with a weight average molecular weight of from about 1,000 to about 65,000, said polymer containing at least some monomer repeat units with a first, photosensitivity-imparting substituent which enables crosslinking or chain extension of the polymer upon exposure to actinic radiation, said polymer also containing a second, thermal sensitivity-imparting substituent which enables further polymerization of the polymer upon exposure to temperatures of about 140°C and higher.

Copending application U.S. Serial No. 08/697,761 discloses a process which comprises reacting a defined polymer with (i) a formaldehyde source, and (ii) an unsaturated acid in the presence of an acid catalyst, thereby forming a curable polymer with unsaturated ester groups.

Copending application U.S. Serial No. 08/705,479 discloses a process which comprises reacting a haloalkylated aromatic polymer with a material selected from the group consisting of unsaturated ester salts, alkoxide salts, alkylcarboxylate salts, and mixtures thereof, thereby forming a curable polymer having functional groups corresponding to the selected salt.

Copending application U.S. Serial No. 08/705,376 discloses a composition which comprises a mixture of (A) a first component comprising a defined polymer, at least some of the monomer repeat units of which have at least one photosensitivity-imparting group thereon, said polymer having a first degree of photosensitivity-imparting group substitution and (B) a second component which comprises either (1) a polymer having a second degree of photosensitivity-imparting group substitution or (2) a reactive diluent having at least one photosensitivity-imparting group per molecule and having a fourth degree of photosensitivity-imparting group substitution.

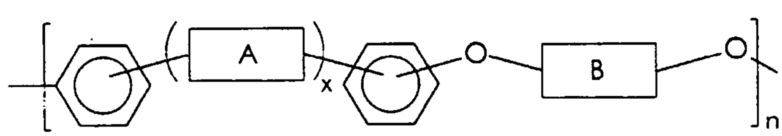
Copending application U.S. Serial No. 08/705,372 discloses a composition which comprises a defined polymer containing at least some monomer repeat units with photosensitivity-imparting substituents which enable crosslinking or chain extension of the polymer upon exposure to actinic radiation, wherein said photosensitivity-imparting substituents are allyl ether groups, epoxy groups, or mixtures thereof.

Copending application U.S. Serial No. 08/697,760 discloses a composition which comprises a polymer containing at least some monomer repeat units with water-solubility-imparting substituents and at least some monomer repeat units with photosensitivity-imparting substituents which enable crosslinking or chain extension of the polymer upon exposure to actinic radiation.

While known compositions and processes are suitable for their intended purposes, a need remains for improved materials suitable for microelectronics applications. A need also remains for improved ink jet printheads. Further, there is a need for photopatternable polymeric materials which are heat stable, electrically insulating, and mechanically robust. Additionally, there is a need for photopatternable polymeric materials which are chemically inert with respect to the materials that might be employed in ink jet ink compositions. There is also a need for photopatternable polymeric materials which exhibit low shrinkage during post-cure steps in microelectronic device fabrication processes. In addition, a need remains for photopatternable polymeric materials which exhibit a relatively long shelf life. Further, there is a need for photopatternable polymeric materials which can be patterned with relatively low photo-exposure energies. Additionally, a need remains for photopatternable polymeric materials which, in the cured form, exhibit good solvent resistance. There is also a need for photopatternable polymeric materials which, when applied to microelectronic devices by spin casting techniques and cured, exhibit reduced edge bead and no apparent lips and dips. Further, a need remains for processes for preparing photopatternable polymeric materials with high aspect ratios at high resolutions by the incorporation of polymerizable groups and/or cross-linking sites pendant to the polymers. Additionally, there is

a need for processes for preparing photopatternable polymers having unsaturated ester groups pendant to the polymer chains and processes for preparing intermediate materials in the synthesis of photopatternable polymers having unsaturated ester groups pendant to the polymer chains. There is also a need for processes for preparing photopatternable polymers having haloalkyl groups pendant to the polymer chains. Further, a need remains for processes for preparing polymers having haloalkyl groups pendant to the polymer chains by methods which do not require the use of hazardous materials such as bis-chloromethyl ether. In addition, there remains a need for photopatternable polymeric materials which have relatively low dielectric constants. Further, there is a need for photopatternable polymeric materials which exhibit reduced water sorption. Additionally, a need remains for photopatternable polymeric materials which exhibit improved hydrolytic stability, especially upon exposure to alkaline solutions. A need also remains for photopatternable polymeric materials which are stable at high temperatures, typically greater than about 150°C. There is also a need for photopatternable polymeric materials which either have high glass transition temperatures or are sufficiently crosslinked that there are no low temperature phase transitions subsequent to photoexposure. Further, a need remains for photopatternable polymeric materials with low coefficients of thermal expansion. There is a need for polymers which are thermally stable, patternable as thick films of about 30 microns or more, exhibit low T_g prior to photoexposure, have low dielectric constants, are low in water absorption, have low coefficients of expansion, have desirable mechanical and adhesive characteristics, and are generally desirable for interlayer dielectric applications, including those at high temperatures, which are also photopatternable. There is also a need for photoresist compositions with good to excellent processing characteristics.

According to one aspect of the present invention, there is provided a process which comprises reacting a polymer of the formula



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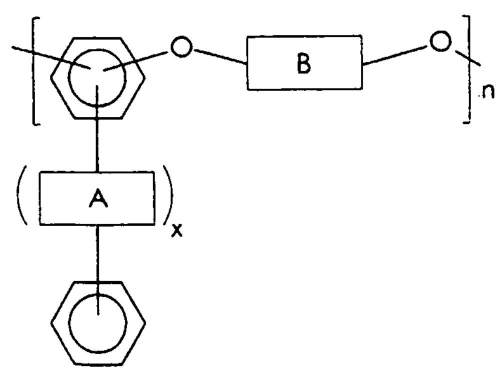
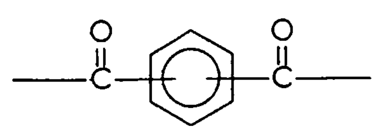
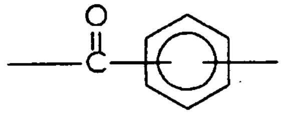
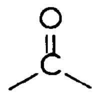
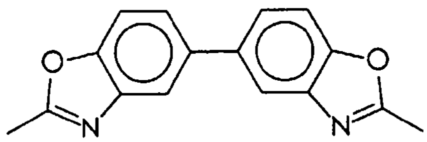


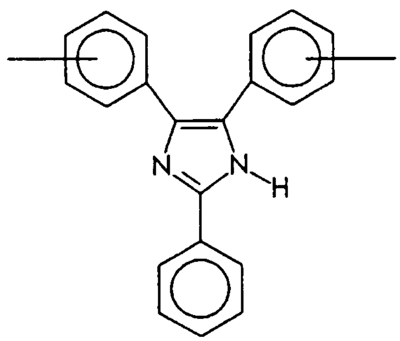
wherein x is an integer of 0 or 1, A is

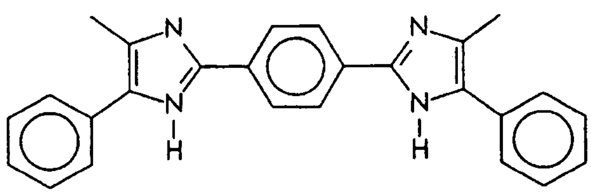








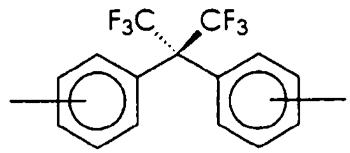


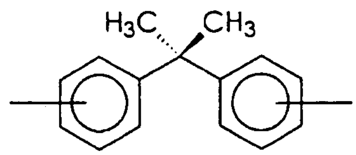


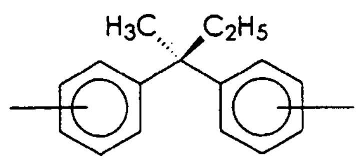
-O-,

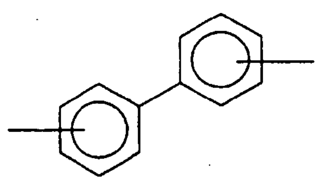
$-C(CH_3)_2-$,

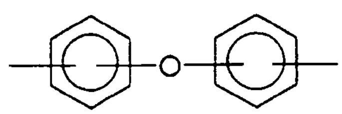
or mixtures thereof, B is

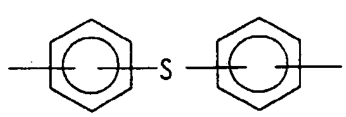


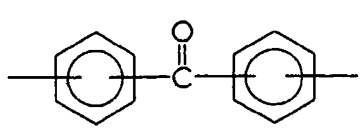


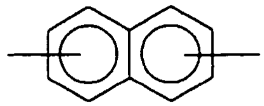












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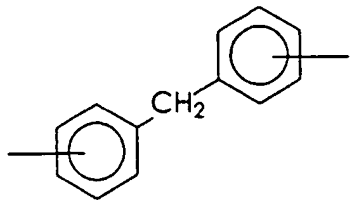

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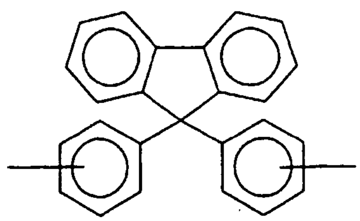

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$$-(CH_2)_v-$$

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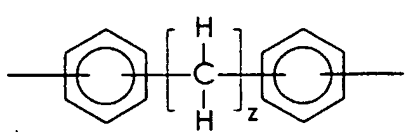
wherein v is an integer of from 1 to about 20,



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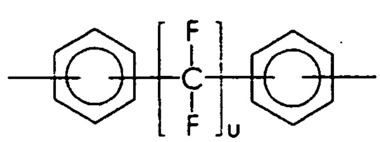
wherein z is an integer of from 2 to about 20,



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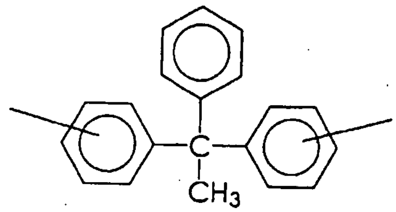
wherein u is an integer of from 1 to about 20,



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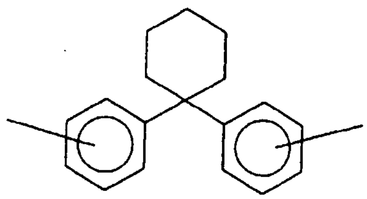

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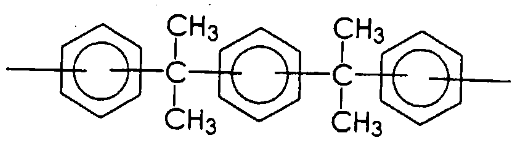

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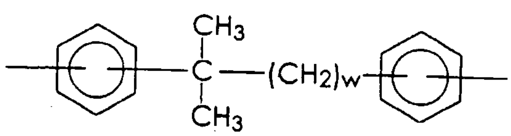

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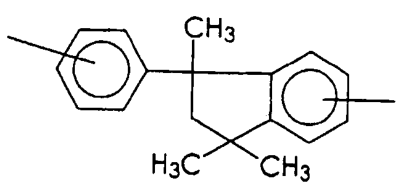
wherein w is an integer of from 1 to about 20,



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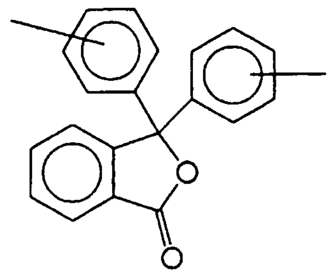

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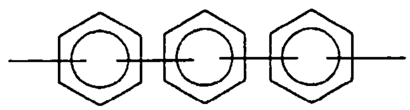

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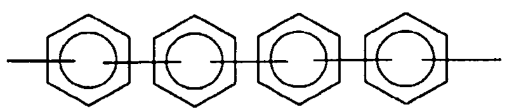

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or mixtures thereof, and n is an integer representing the number of repeating monomer units, with an acetyl halide and dimethoxymethane in the presence of a halogen-containing Lewis acid catalyst and methanol, thereby forming a haloalkylated polymer.

According to another aspect of the present invention, there is provided a process comprising the step of causing the polymer to become crosslinked or chain extended through the photosensitivity-imparting groups.

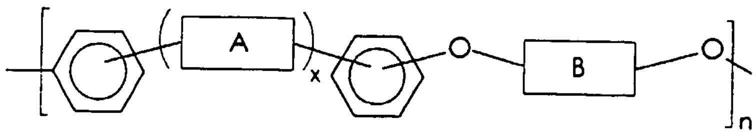
According to another aspect of the present invention, there is provided a process for forming a thermal ink jet printhead comprising the steps of: (a) depositing a layer comprising a polymer onto a lower substrate in which one surface thereof has an array of heating elements and addressing electrodes having terminal ends formed thereon; (b) exposing the layer to actinic radiation in an imagewise pattern such that the polymer in exposed areas becomes crosslinked or chain extended and the polymer in unexposed areas does not become crosslinked or chain extended, wherein the unexposed areas correspond to areas of the lower substrate having thereon the heating elements and the terminal ends of the addressing electrodes; (c) removing the polymer from the unexposed areas, thereby forming recesses in the layer, said recesses exposing the heating elements and the terminal ends of the addressing electrodes; (d) providing an upper substrate with a set of parallel grooves for subsequent use as ink channels and a recess for subsequent use as a manifold, the grooves being open at one end for serving as droplet emitting nozzles; and (e) aligning, mating, and bonding the upper and lower substrates together to form a printhead with the grooves in the upper substrate being aligned with the heating elements in the lower substrate to form droplet emitting nozzles, thereby forming a thermal ink jet printhead.

Figure 1 is an enlarged schematic isometric view of an example of a printhead mounted on a daughter board showing the droplet emitting nozzles.

Figure 2 is an enlarged cross-sectional view of Figure 1 as viewed along the line 2-2 thereof and showing the electrode passivation and ink flow path between the manifold and the ink channels.

Figure 3 is an enlarged cross-sectional view of an alternate embodiment of the printhead in Figure 1 as viewed along the line 2-2 thereof.

The present invention is directed to a process for preparing polymers having haloalkyl functional groups. The starting polymers for the preparation processes of the present invention are of the following formula:



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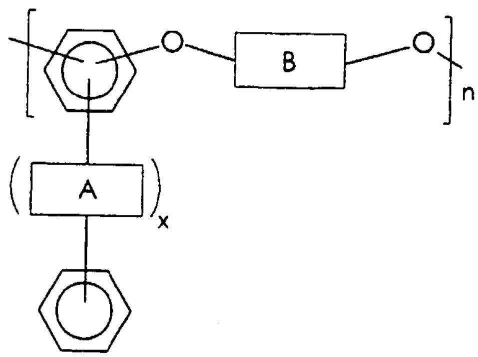
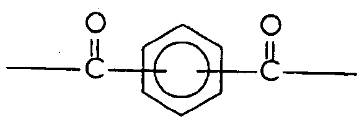


wherein x is an integer of 0 or 1, A is



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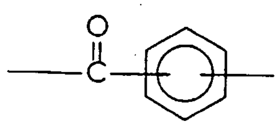

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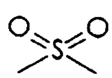

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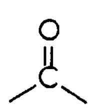

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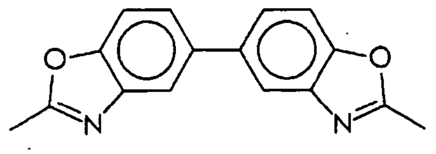
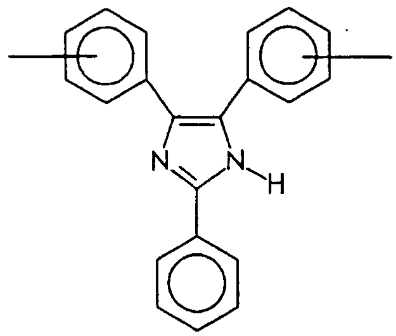
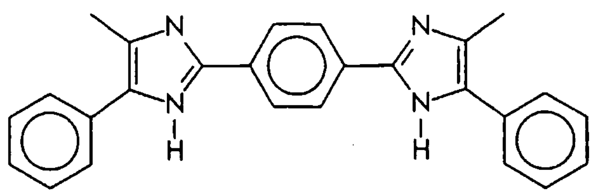


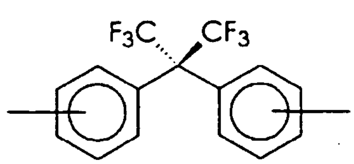


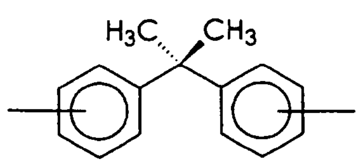


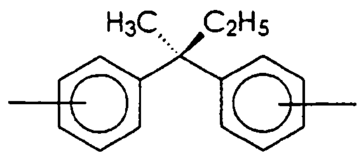
-O-,

$-C(CH_3)_2-$,

or mixtures thereof, B is



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C2H5

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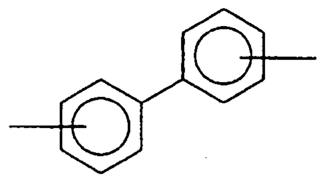

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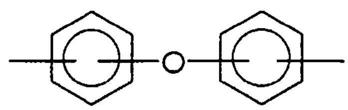
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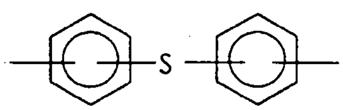
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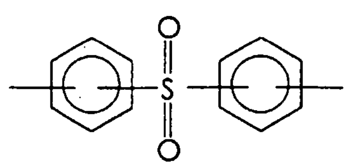
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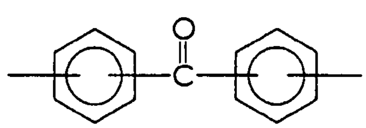
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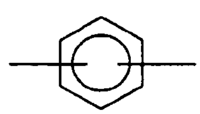

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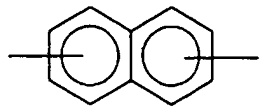

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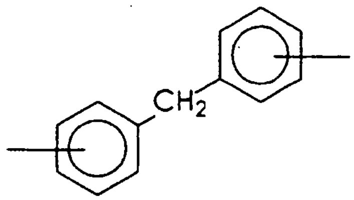

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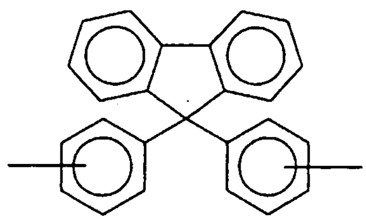

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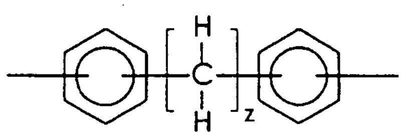
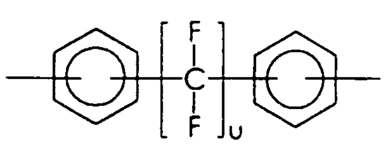
$$-(CH_2)_v-$$

,

wherein v is an integer of from 1 to about 20, and preferably from 1 to about 10,

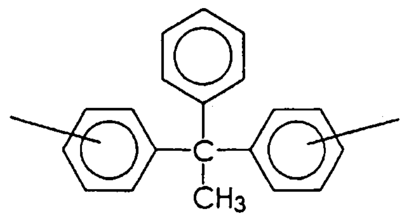


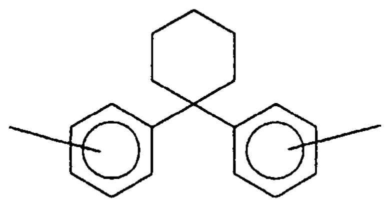
wherein z is an integer of from 2 to about 20, and preferably from 2 to about 10,

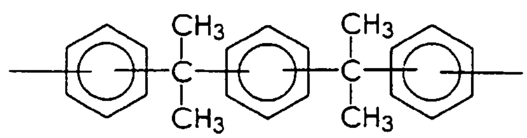


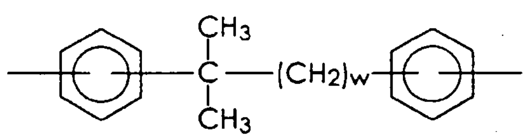
,

wherein u is an integer of from 1 to about 20, and preferably from 1 to about 10,

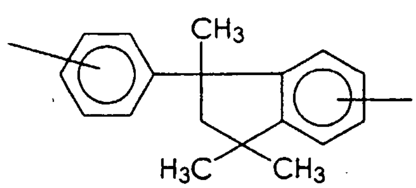


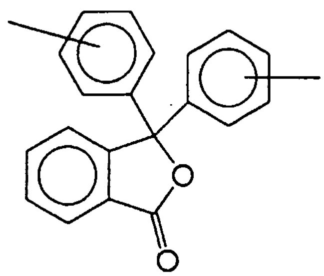


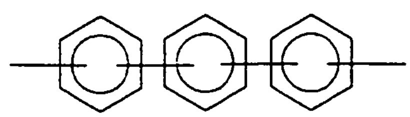


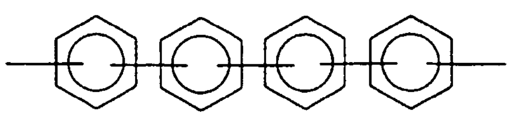


wherein w is an integer of from 1 to about 20, and preferably from 1 to about 10,









other similar bisphenol derivatives, or mixtures thereof, and n is an integer representing the number of repeating monomer units. The value of n is such that the weight average molecular weight of the material typically is from about 1,000 to about 100,000, preferably from about 1,000 to about 65,000, more preferably from about 1,000 to about 40,000, and even more preferably from about 3,000 to about 25,000, although the weight average molecular weight can be outside these ranges. Preferably, n is an integer of from about 2 to about 70, more preferably from about 5 to about 70, and even more preferably from about 8 to about 50, although the value of n can be outside these ranges. The phenyl groups and the A and/or B groups may also be substituted, although the presence of two or more substituents on the B group ortho to the oxygen groups can render substitution difficult. Substituents can be present on the polymer either prior to or subsequent to the placement of haloalkyl functional groups thereon. Substituents can also be placed on the polymer during the process of placement of haloalkyl functional groups thereon. Haloalkyl groups can also be further reacted to place desired substituents on the polymer. Examples of suitable substituents include (but are not limited to) alkyl groups, including saturated, unsaturated, and cyclic alkyl groups, preferably with from 1 to about 6 carbon atoms, substituted alkyl groups, including saturated, unsaturated, and cyclic substituted alkyl groups, preferably with from 1 to about 6 carbon atoms, aryl groups, preferably with from 6 to about 24 carbon atoms, substituted aryl groups, preferably with from 6 to about 24 carbon atoms, arylalkyl groups, preferably with from 7 to about 30 carbon atoms, substituted arylalkyl groups, preferably with from 7 to about 30 carbon atoms, alkoxy groups, preferably with from 1 to about 6 carbon atoms, substituted alkoxy groups, preferably with from 1 to about 6 carbon atoms, aryloxy groups, preferably with from 6 to about 24 carbon atoms, substituted aryloxy groups, preferably with from 6 to about 24 carbon atoms, arylalkyloxy groups, preferably with from 7 to about 30 carbon atoms, substituted arylalkyloxy groups, preferably with from 7 to about 30 carbon atoms, hydroxy groups, amine groups, imine groups, ammonium groups, pyridine groups, pyridinium groups, ether groups, ester groups, amide groups, carbonyl groups, thiocarbonyl groups, sulfate groups, sulfonate groups, sulfide groups, sulfoxide groups, phosphine groups, phosphonium groups, phosphate groups, mercapto groups, nitroso groups, sulfone groups, acyl groups, acid anhydride groups, azide groups, and the like, wherein the substituents on the substituted alkyl groups, substituted aryl groups, substituted arylalkyl groups, substituted alkoxy groups, substituted aryloxy groups, and substituted arylalkyloxy groups can be (but are not limited to) hydroxy groups, amine groups, imine groups, ammonium groups, pyridine groups, pyridinium groups, ether groups, aldehyde groups, ketone groups, ester groups, amide groups, carboxylic acid groups, carbonyl groups, thiocarbonyl groups, sulfate groups, sulfonate groups, sulfide groups, sulfoxide groups, phosphine groups, phosphonium groups, phosphate groups, cyano groups, nitrile groups, mercapto groups, nitroso groups, halogen atoms, nitro groups, sulfone groups, acyl groups, acid anhydride groups, azide groups, mixtures thereof, and the like wherein two or more substituents can be joined together to form a ring. Processes for the preparation of these materials are known, and disclosed

in, for example, P. M. Hergenrother, *J. Macromol. Sci. Rev. Macromol. Chem.*, ***C19***(1), 1-34 (1980); P. M. Hergenrother, B. J. Jensen, and S. J. Havens, *Polymer*, ***29***, 358 (1988); B. J. Jensen and P.M. Hergenrother, "High Performance Polymers," Vol. 1, No. 1) page 31 (1989), "Effect of Molecular Weight on Poly(arylene ether ketone) Properties"; V. Percec and B. C. Auman, *Makromol. Chem.* ***185***, 2319 (1984); "High Molecular Weight Polymers by Nickel Coupling of Aryl Polychlorides," I. Colon, G. T. Kwaiatkowski, *J. of Polymer Science, Part A, Polymer Chemistry*, ***28***, 367 (1990); M. Ueda and T. Ito, *Polymer* J., ***23***(4), 297 (1991); "Ethynyl-Terminated Polyarylates: Synthesis and Characterization, " S. J. Havens and P. M. Hergenrother, *J. of Polymer Science: Polymer Chemistry Edition*, ***22***, 3011 (1984); "Ethynyl-Terminated Polysulfones: Synthesis and Characterization," P. M. Hergenrother, *J. of Polymer Science: Polymer Chemistry Edition*, ***20***, 3131 (1982); K. E. Dukes, M. D. Forbes, A. S. Jeevarajan, A. M. Belu, J. M.DeDimone, R. W. Linton, and V. V. Sheares, *Macromolecules*, ***29***, 3081 (1996); G. Hougham, G. Tesoro, and J. Shaw, *Polym. Mater. Sci. Eng.*, ***61***, 369 (1989); V. Percec and B. C. Auman, *Makromol. Chem*, ***185***, 617 (1984); "Synthesis and characterization of New Fluorescent Poly(arylene ethers)," S. Matsuo, N. Yakoh, S. Chino, M. Mitani, and S. Tagami, *Journal of Polymer Science: Part A: Polymer Chemistry*, ***32***, 1071 (1994); "Synthesis of a Novel Naphthalene-Based Poly(arylene ether ketone) with High Solubility and Thermal Stability," Mami Ohno, Toshikazu Takata, and Takeshi Endo, *Macromolecules*, ***27***, 3447 (1994); "Synthesis and Characterization of New Aromatic Poly(ether ketones)," F. W. Mercer, M. T. Mckenzie, G. Merlino, and M. M. Fone, J. *of Applied Polymer Science*, ***56***, 1397 (1995); H. C. Zhang, T. L. Chen, Y. G. Yuan, Chinese Patent CN 85108751 (1991); "Static and laser light scattering study of novel thermoplastics. 1. Phenolphthalein poly(aryl ether ketone)," C. Wu, S. Bo, M. Siddiq, G. Yang and T. Chen, *Macromolecules*, ***29***, 2989 (1996); "Synthesis of t-Butyl-Substituted Poly(ether ketone) by Nickel-Catalyzed Coupling Polymerization of Aromatic Dichloride", M. Ueda, Y. Seino, Y. Haneda, M. Yoneda, and J.-I. Sugiyama, *Journal of Polymer Science: Part A: Polymer Chemistry*, ***32***, 675 (1994); "Reaction Mechanisms: Comb-Like Polymers and Graft Copolymers from Macromers 2. Synthesis, Characterzation and Homopolymerization of a Styrene Macromer of Poly(2,6-dimethyl-1,4-phenylene Oxide)," V. Percec, P. L. Rinaldi, and B. C. Auman, *Polymer Bulletin*, ***10***, 397 (1983); *Handbook of Polymer Synthesis Part A*, Hans R. Kricheldorf, ed., Marcel Dekker, Inc., New York-Basel-Hong Kong (1992); and "Introduction of Carboxyl Groups into Crosslinked Polystyrene," C. R. Harrison, P. Hodge, J. Kemp, and G. M. Perry, *Die Makromolekulare Chemie*, ***176***, 267 (1975).

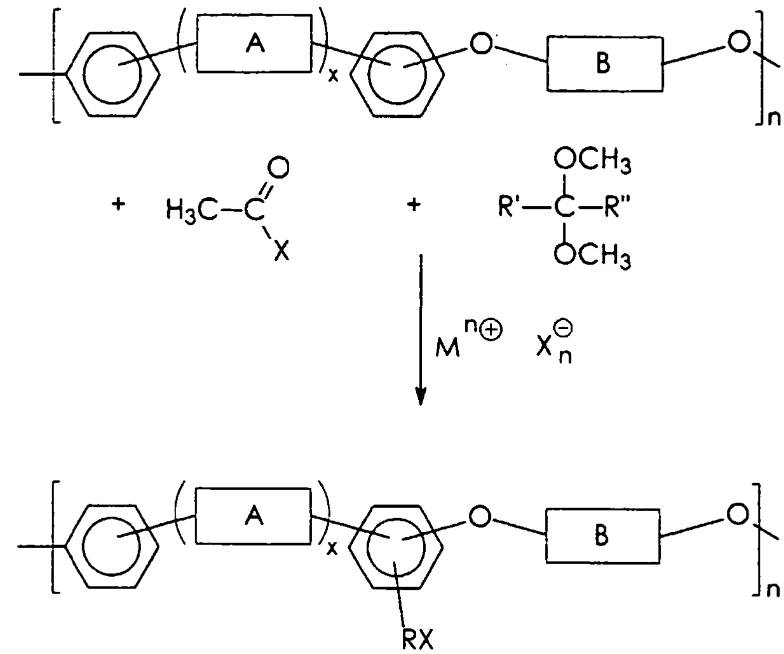
For applications wherein the polymer is to be used as a layer in a thermal ink jet printhead, the polymer preferably has a number average molecular weight of from about 3,000 to about 20,000, more preferably from about 3,000 to about 10,000, and even more preferably from about 3,500 to about 5,500, although the molecular weight can be outside this range.

The haloalkylation of the polymer is accomplished by reacting the polymer with an acetyl halide, such as acetyl chloride, and dimethoxymethane in the presence of a halogen-containing Lewis acid catalyst, such as those of the general formula

$$M^{n\oplus} X_n$$

wherein n is an integer of 1, 2, 3, 4, or 5, M represents a boron atom or a metal atom, such as tin, aluminum, zinc, antimony, iron (III), gallium, indium, arsenic, mercury, copper, platinum, palladium, or the like, and X represents a halogen atom, such as fluorine, chlorine, bromine, or iodine, with specific examples including $SnCl_4$, $AlCl_3$, $ZnCl_2$, $AlBr_3$, BF_3, SbF_5, FeI_3, $GaBr_3$, $InCl_3$, AsI_5, $HgBr_2$, $CuCl$, $PdCl_2$, or $PtBr_2$. Methanol is added to generate hydrohalic acid catalytically; the hydrohalic acid reacts with dimethoxymethane to form halomethyl methyl ether. Care must be taken to avoid cross-linking of the haloalkylated polymer. Typically, the reactants are present in relative amounts by weight of about 35.3 parts acetyl halide, about 37 parts dimethoxymethane, about 1.2 parts methanol, about 0.3 parts Lewis acid catalyst, about 446 parts 1,1,2,2-tetrachloroethane, and about 10 to 20 parts polymer. 1,1,2,2-Tetrachlororethane is a suitable reaction solvent. Dichloromethane is low boiling, and consequently the reaction is slow in this solvent unless suitable pressure equipment is used.

The general reaction scheme is as follows:



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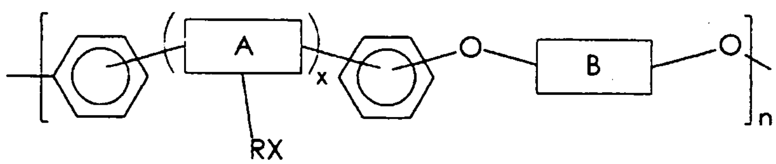

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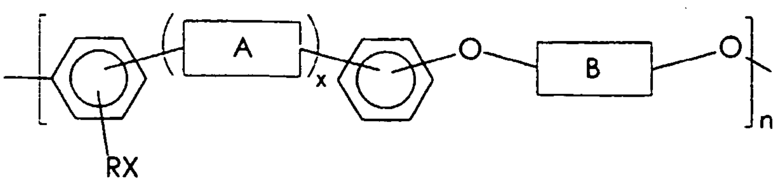

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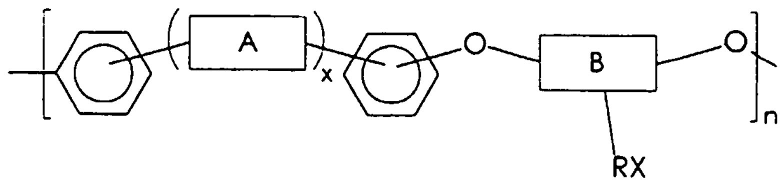
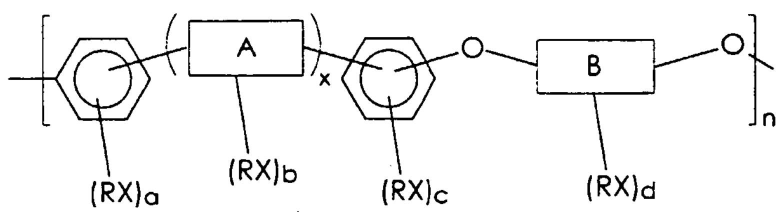


wherein R' and R" each, independently of the other, can be (but are not limited to) hydrogen atoms, alkyl groups, including saturated, unsaturated, and cyclic alkyl groups, preferably with from 1 to about 11 carbon atoms, substituted alkyl groups, preferably with from 1 to about 11 carbon atoms, aryl groups, preferably with from 6 to about 11 carbon atoms, substituted aryl groups, preferably with from 6 to about 11 carbon atoms, arylalkyl groups, preferably with from 7 to about 11 carbon atoms, substituted arylalkyl groups, preferably with from 7 to about 11 carbon atoms, and the like. The resulting material is of the general formula



wherein n is an integer of 1, 2, 3, 4, or 5, R is an alkyl group, including both saturated, unsaturated, linear, branched, and cyclic alkyl groups, preferably with from 1 to about 11 carbon atoms, more preferably with from 1 to about 5 carbon atoms, even more preferably with from 1 to about 3 carbon atoms, and most preferably with 1 carbon atom, or a substituted alkyl group, an arylalkyl group, preferably with from 7 to about 29 carbon atoms, more preferably with from 7 to about 17 carbon atoms, even more preferably with from 7 to about 13 carbon atoms, and most preferably with from 7 to about 9 carbon atoms, or a substituted arylalkyl group, and X is a halogen atom, such as fluorine, chlorine, bromine, or iodine, a, b, c, and d are each integers of 0, 1, 2, 3, or 4, provided that at least one of a, b, c, and d is equal to or greater than 1 in at least some of the monomer repeat units of the polymer, and n is an integer representing the number of repeating monomer units. Examples of suitable substituents on the substituted alkyl, aryl, and arylalkyl groups include (but are not limited to) alkyl groups, including saturated, unsaturated, linear, branched, and cyclic alkyl groups, preferably with from 1 to about 6 carbon atoms, substituted alkyl groups, preferably with from 1 to about 6 carbon atoms, aryl groups, preferably with from 6 to about 24 carbon atoms, substituted aryl groups, preferably with from 6 to about 24 carbon atoms, arylalkyl groups, preferably with from 7 to about 30 carbon atoms, substituted arylalkyl groups, preferably with from 7 to about 30 carbon atoms, alkoxy groups, preferably with from 1 to about 6 carbon atoms, substituted alkoxy groups, preferably with from 1 to about 6 carbon atoms, aryloxy groups, preferably with from 6 to about 24 carbon atoms, substituted aryloxy groups, preferably with from 6 to about 24 carbon atoms, arylalkyloxy groups, preferably with from 7 to about 30 carbon atoms, substituted arylalkyloxy groups, preferably with from 7 to about 30 carbon atoms, amine groups, imine groups, ammonium groups, pyridine groups, pyridinium groups, ether groups, ester groups, amide groups, carbonyl groups, thiocarbonyl groups, sulfate groups, sulfonate groups, sulfide groups, sulfoxide groups, phosphine groups, phosphonium groups, phosphate groups, mercapto groups, nitroso groups, sulfone groups, acyl groups, acid anhydride groups, azide groups, and the like, wherein the substituents on the substituted alkyl groups, substituted aryl groups, substituted arylalkyl groups, substituted alkoxy groups, substituted aryloxy groups, and substituted arylalkyloxy groups can be (but are not limited to) hydroxy groups, amine groups, imine groups, ammonium groups, pyridine groups, pyridinium groups, ether groups, aldehyde groups, ketone groups, ester groups, amide groups, carboxylic acid groups, carbonyl groups, thiocarbonyl groups, sulfate groups, sulfonate groups, sulfide groups, sulfoxide groups, phosphine groups, phosphonium groups, phosphate groups, cyano groups, nitrile groups, mercapto groups, nitroso groups, halogen atoms, nitro groups, sulfone groups, acyl groups, acid anhydride groups, azide groups, mixtures thereof, and the like, wherein two or more substituents can be joined together to form a ring. Substitution is generally random, although the substituent often indicates a preference for the B group, and any given monomer repeat unit may have no haloalkyl substituents, one haloalkyl substituent, or two or more haloalkyl substituents.

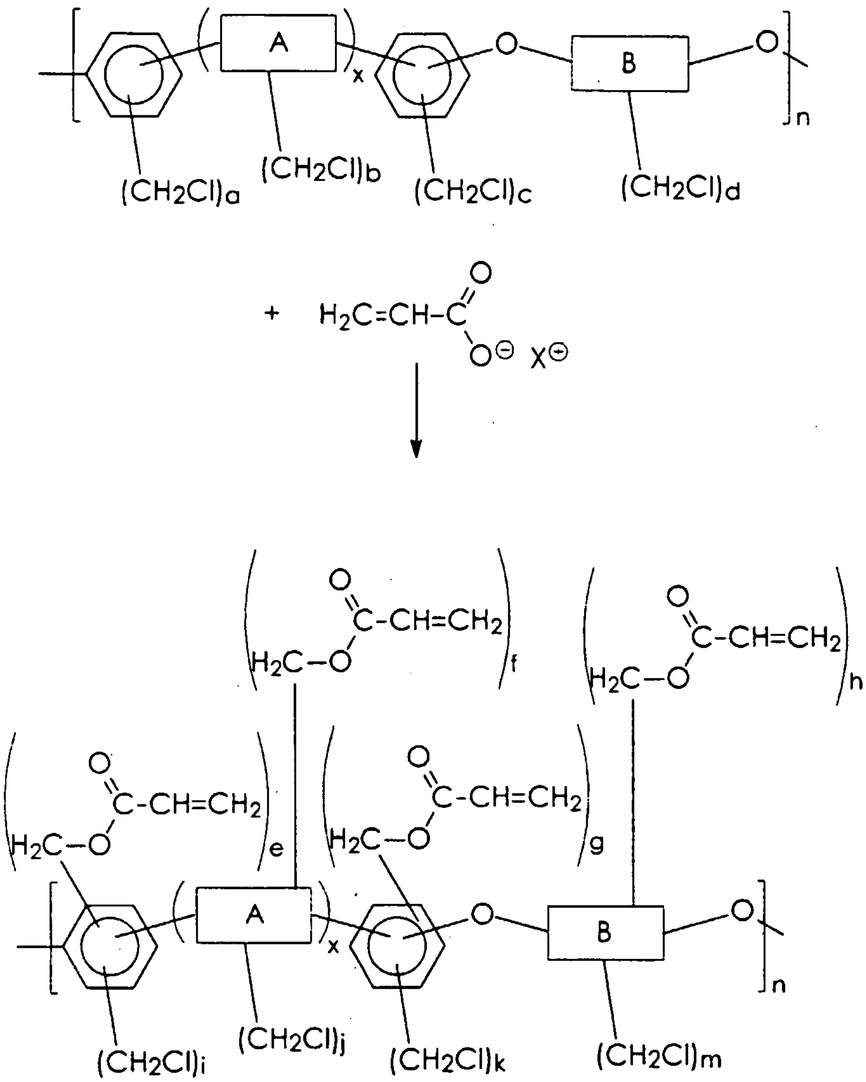
Typical reaction temperatures are from about 60 to about 120°C, and preferably from about 80 to about 110°C, although the temperature can be outside these ranges. Typical reaction times are from about 1 to about 10 hours, and preferably from about 2 to about 4 hours, although the time can be outside these ranges. Longer reaction times generally result in higher degrees of haloalkylation. When the haloalkylated polymer is used as an intermediate material in the synthesis of polymers substituted with photoactive groups, higher degrees of haloalkylation generally enable higher degrees of substitution with photoactive groups and thereby enable greater photosensitivity of the polymer. Different degrees of haloalkylation may be desirable for different applications. When the material is used as an intermediate in the synthesis of the polymer substituted with photosensitivity-imparting groups, too high a degree of substitution may lead to excessive sensitivity, resulting in crosslinking or chain extension of both exposed and unexposed polymer material when the material is exposed imagewise to activating radiation, whereas too low a degree of substitution may be undesirable because of resulting unnecessarily long exposure times or unnecessarily high exposure energies. For applications wherein the photopatternable polymer is to be used as a layer in a thermal ink jet printhead, the degree of substitution (i.e., the average number of photosensitivity-imparting groups per monomer repeat unit repeat unit) preferably is from about 0.5 to about 1.2, and more preferably from about 0.7 to about 0.8, although the degree of substitution can be outside these ranges for ink jet printhead applications. This amount of substitution corresponds to from about 0.8 to about 1.3 milliequivalents of photosensitivity-imparting groups per gram of resin. When the haloalkyl groups are eventually to be substituted by photosensitivity-imparting groups, the degree of haloalkylation is typically from about 0.25 to about 2, and, when it is desired to speed up the substitution reaction, preferably is from about 1 to about 2, and even more preferably from about 1.5 to about 2, although the degree of haloalkylation can be outside these ranges.

The halomethylated polymer can also be used as a photoresist in its own right provided that a sufficiently high energy source is used to expose the polymer films. Electron beams, ultraviolet lasers, deep ultraviolet sources between 200 and 260 nanometers, and X-rays are generally sufficiently high in energy for the intended purpose of exposing and crosslinking halomethylated polymer films. The mechanism of crosslinking is believed to be the generation of benzylic type radicals which can then couple to render the polymer insoluble.

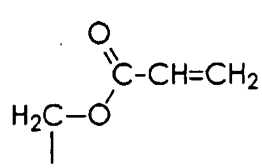
Haloalkylated polymers can also find uses in membrane technology, especially when reacted with tertiary amines to generate cationic sites. For this purpose, the amount of haloalkylation typically is from about 1 to about 2 milliequivalents of bound cationic groups per gram of resin.

The haloalkylated polymer can be further reacted to replace at least some of the haloalkyl groups with photosensitivity-imparting groups such as unsaturated ester, ether, or alkylcarboxymethylene groups if desired. The haloalkylated polymer can be substituted with these groups by reacting the haloalkylated polymer with an unsaturated ester, alkoxide, or alkylcarboxylate salt in solution. Examples of suitable reactants include selected salts of Groups IA, IIB, IIIB, IVB, VB, VIB, VIIB, VIIIB, IB, IIB, IIIA, IVA, of the periodic table with the appropriate unsaturated ester, such as the ester salts of acrylic acid, methacrylic acid, cinnamic acid, crotonic acid, ethacrylic acid, oleic acid, linoleic acid, maleic acid, fumaric acid, itaconic acid, citraconic acid, phenylmaleic acid, 3-hexene-1,6-dicarboxylic acid, and the like, or the appropriate alkoxide or alkylcarboxylate, with specific examples including sodium, potassium, quaternary ammonium, phosphonium, and the like salts of acrylate, methacrylate, cinnamate, acetate, methoxide, and the like. Examples of solvents suitable for the reaction include polar aprotic solvents such as N,N-dimethylacetamide, dimethylsulfoxide, and N-methylpyrrolidinone, dimethylformamide. Typically, the reactants are present in relative amounts with respect to each other by weight of about 10 parts haloalkylated polymer, about 66.5 parts solvent, and about 5.7 parts unsaturated ester, alkoxide, and/or alkylcarboxylate salt.

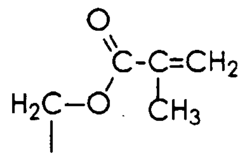
The general reaction scheme, illustrated below for the acryloylation of the chloromethylated polymer, is as follows:



wherein X is any suitable cation, such as sodium, potassium, or the like, a, b, c, d, e, f, g, h, i, j, k, and m are each integers of 0, 1, 2, 3, or 4, provided that the sum of i+e is no greater than 4, the sum of j+f is no greater than 4, the sum of k+g is no greater than 4, and the sum of m+h is no greater than 4, provided that at least one of a, b, c, and d is equal to or greater than 1 in at least some of the monomer repeat units of the polymer, and provided that at least one of e, f, g, and h is equal to at least 1 in at least some of the monomer repeat units of the polymer, and n is an integer representing the number of repeating monomer units. In the corresponding reaction with the methacrylate salt, the reaction proceeds as shown above except that the

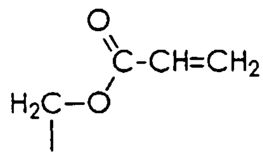


groups shown above are replaced with

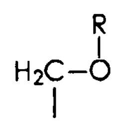


groups.

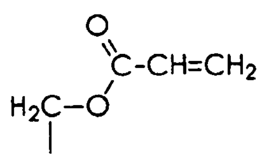
Ether groups and alkylcarboxymethylene groups can also be placed on the haloalkylated polymer by a process analogous to that employed to place unsaturated ester groups on the haloalkylated polymer, except that the corresponding alkylcarboxylate or alkoxide salt is employed as a reactant. In the corresponding reaction with the alkoxide salt, the reaction proceeds as shown above except that the



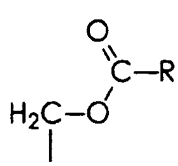
groups shown above are replaced with



groups. Suitable ether groups include those wherein R is an alkyl group, preferably with from 1 to about 30 carbon atoms, more preferably with from 1 to about 15 carbon atoms, and most preferably with 1 carbon atom. In the corresponding reaction with the alkylcarboxylate salt, the reaction proceeds as shown above except that the



groups shown above are replaced with



groups, wherein R is an alkyl group (including saturated, unsaturated, and cyclic alkyl groups), preferably with from 1 to about 30 carbon atoms, more preferably with from 1 to about 6 carbon atoms, a substituted alkyl group, an aryl group, preferably with from 6 to about 30 carbon atoms, more preferably with from 1 to about 2 carbon atoms, a substituted aryl group, an arylalkyl group, preferably with from 7 to about 35 carbon atoms, more preferably with from 7 to about 15 carbon atoms, or a substituted arylalkyl group, wherein the substituents on the substituted alkyl, aryl,

and arylalkyl groups can be (but are not limited to) alkoxy groups, preferably with from 1 to about 6 carbon atoms, aryloxy groups, preferably with from 6 to about 24 carbon atoms, arylalkyloxy groups, preferably with from 7 to about 30 carbon atoms, hydroxy groups, amine groups, imine groups, ammonium groups, pyridine groups, pyridinium groups, ether groups, ester groups, amide groups, carbonyl groups, thiocarbonyl groups, sulfate groups, sulfonate groups, sulfide groups, sulfoxide groups, phosphine groups, phosphonium groups, phosphate groups, mercapto groups, nitroso groups, sulfone groups, acyl groups, acid anhydride groups, azide groups, and the like, wherein two or more substituents can be joined together to form a ring.

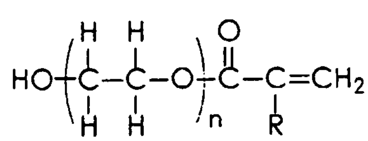
Higher degrees of haloalkylation generally enable higher degrees of substitution with unsaturated ester, ether, or alkylcarboxymethylene groups and thereby enable greater photosensitivity of the polymer. Different degrees of substitution with unsaturated ester, ether, or alkylcarboxymethylene groups may be desirable for different applications. Too high a degree of substitution may lead to excessive sensitivity, resulting in crosslinking or chain extension of both exposed and unexposed polymer material when the material is exposed imagewise to activating radiation, whereas too low a degree of substitution may be undesirable because of resulting unnecessarily long exposure times or unnecessarily high exposure energies. For applications wherein the photopatternable polymer is to be used as a layer in a thermal ink jet printhead, the degree of substitution (i.e., the average number of unsaturated ester, ether, or alkylcarboxymethylene groups per monomer repeat unit) preferably is from about 0.5 to about 1.2, and more preferably from about 0.65 to about 0.8, although the degree of substitution can be outside these ranges for ink jet printhead applications. Optimum amounts of substitution with unsaturated ester, ether, or alkylcarboxymethylene groups are from about 0.8 to about 1.3 milliequivalents of unsaturated ester per gram of resin.

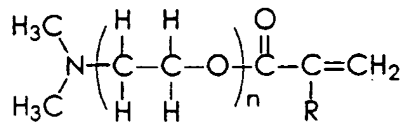
Some or all of the haloalkyl groups can be replaced with unsaturated ester, ether, or alkylcarboxymethylene substituents. Longer reaction times generally lead to greater degrees of substitution of haloalkyl groups with unsaturated ester, ether, or alkylcarboxymethylene substituents.

Typical reaction temperatures are from about 20 to about 35°C, and preferably about 25°C, although the temperature can be outside this range. Typical reaction times are from about 30 minutes to about 15 days, and preferably from about 2 hours to about 2 days, although the time can be outside these ranges. The reaction time can be reduced with the use of a catalyst, such as Adogen 464 (available from Aldrich Chemical Co., Milwaukee, WI, or from Ashland Oil Co.), a long chain quaternary ammonium chloride salt, or the like. Adogen 464 is used at approximately 0.4 weight percent with respect to resin solids, and this catalyst results in a doubling of the reaction rate. Adogen 464 is sometimes difficult to remove from the product even after several water and methanol washes. Consequently, this catalyst sometimes results in cloudy photoresist solutions. The reaction can be accelerated slightly by the addition of 0.4 weight percent water, and can be inhibited by the addition of the same amount of methanol.

The haloalkylated polymer can be allyl ether substituted or epoxidized by first reacting the haloalkylated polymer with an unsaturated alcohol salt, such as an allyl alcohol salt, in solution. A suitable reaction scheme is described in US Serial No. 08/705,372. Examples of suitable unsaturated alcohol salts and allyl alcohol salts include sodium 2-allylphenolate, sodium 4-allylphenolate, sodium allyl alcoholate, corresponding salts with lithium, potassium, cesium, rubidium, ammonium, quaternary alkyl ammonium compounds, and the like. An unsaturated alcohol salt can be generated by the reaction of the alcohol with a base, such as sodium hydride, sodium hydroxide, or the like. The salt displaces the halide of the haloalkyl groups at between about 25 and about 100°C. Examples of solvents suitable for the reaction include polar aprotic solvents such as N,N-dimethylacetamide, dimethylsulfoxide, N-methylpyrrolidinone, dimethylformamide, tetrahydrofuran, and the like. Typically, the reactants are present in relative amounts with respect to each other of from about 1 to about 50 molar equivalents of unsaturated alcohol salt per haloalkyl group to be substituted, although the relative amounts can be outside this range. Typically, the reactants are present in solution in amounts of from about 5 to about 50 percent by weight solids, and preferably about 10 percent by weight solids, although the relative amounts can be outside this range.

The haloalkylated polymer can be substituted with a photosensitivity-imparting, water-solubility-enhancing (or water-dispersability-enhancing) group by reacting the haloalkylated polymer with an unsaturated amine, phosphine, or alcohol, as for example, described in US Serial No. 08/697,760. Examples of suitable reactants include N,N-dimethyl ethyl methacrylate, N,N-dimethyl ethyl acrylate,

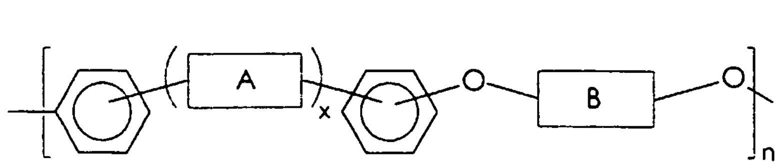




wherein R is H or CH_3 and n is an integer of from 1 to about 50.

Polymers of the above formula can also be hydroxyalkylated by first preparing the haloalkylated derivative and then replacing at least some of the haloalkyl groups with hydroxyalkyl groups. A suitable replacement reaction scheme is described in US Serial No. 08/705,365. For example, the haloalkylated polymer can be hydroxyalkylated by alkaline hydrolysis of the haloalkylated polymer. The hydroxy groups replace the halide atoms in the haloalkyl groups on the polymer; accordingly, the number of carbon atoms in the haloalkyl group generally corresponds to the number of carbon atoms in the hydroxyalkyl group. Examples of suitable reactants include sodium hydroxide, potassium hydroxide, calcium hydroxide, ammonium hydroxide, tetraalkyl ammonium hydroxides, such as tetrabutyl ammonium hydroxide, and the like. Examples of solvents suitable for the reaction include 1,1,2,2-tetrachloroethane, methylene chloride, and water.

In some instances, the terminal groups on the polymer can be selected by the stoichiometry of the polymer synthesis. For example, when a polymer is prepared by the reaction of 4,4'-dichlorobenzophenone and bis-phenol A in the presence of potassium carbonate in N,N-dimethylacetamide, if the bis-phenol A is present in about 7.5 to 8 mole percent excess, the resulting polymer generally is bis-phenol A-terminated (wherein the bis-phenol A moiety may or may not have one or more hydroxy groups thereon), and the resulting polymer typically has a polydispersity (M_w/M_n) of from about 2 to about 3.5. When the bis-phenol A-terminated polymer is subjected to further reactions to place functional groups thereon, such as haloalkyl groups, and/or to convert one kind of functional group, such as a haloalkyl group, to another kind of functional group, such as an unsaturated ester group, the polydispersity of the polymer can rise to the range of from about 4 to about 6. In contrast, if the 4,4'-dichlorobenzophenone is present in about 7.5 to 8 mole percent excess, the reaction time is approximately half that required for the bis-phenol A excess reaction, the resulting polymer generally is benzophenone-terminated (wherein the benzophenone moiety may or may not have one or more chlorine atoms thereon), and the resulting polymer typically has a polydispersity of from about 2 to about 3.5. When the benzophenone-terminated polymer is subjected to further reactions to place functional groups thereon, such as haloalkyl groups, and/or to convert one kind of functional group, such as a haloalkyl group, to another kind of functional group, such as an unsaturated ester group, the polydispersity of the polymer typically remains in the range of from about 2 to about 3.5. Similarly, when a polymer is prepared by the reaction of 4,4'-difluorobenzophenone with either 9,9'-bis(4-hydroxyphenyl)fluorene or bis-phenol A in the presence of potassium carbonate in N,N-dimethylacetamide, if the 4,4'-difluorobenzophenone reactant is present in excess, the resulting polymer generally has benzophenone terminal groups (which may or may not have one or more fluorine atoms thereon). The well-known Carothers equation can be employed to calculate the stoichiometric offset required to obtain the desired molecular weight. (See, for example, William H. Carothers, "An Introduction to the General Theory of Condensation Polymers," *Chem. Rev,* ***8***, 353 (1931) and *J. Amer. Chem. Soc.*, ***51***, 2548 (1929); see also P. J. Flory, *Principles of Polymer Chemistry,* Cornell University Press, Ithaca, New York (1953). More generally speaking, during the preparation of polymers of the formula



the stoichiometry of the polymer synthesis reaction can be adjusted so that the end groups of the polymer are derived from the "A" groups or derived from the "B" groups. Specific functional groups can also be present on these terminal "A" groups or "B" groups, such as ethynyl groups or other thermally sensitive groups, hydroxy groups which are attached to the aromatic ring on an "A" or "B" group to form a phenolic moiety, halogen atoms which are attached to the "A" or "B" group, or the like.

Polymers with end groups derived from the "A" group, such as benzophenone groups or halogenated benzophenone groups, may be preferred for some applications because both the syntheses and some of the reactions of these materials to place substituents thereon may be easier to control and may yield better results with respect to, for example, cost, molecular weight, molecular weight range, and polydispersity (M_w/M_n) compared to polymers with end groups derived from the "B" group, such as bis-phenol A groups (having one or more hydroxy groups on the aromatic rings

thereof) or other phenolic groups. While not being limited to any particular theory, it is believed that the haloalkylation reaction in particular proceeds most rapidly on the phenolic tails when the polymer is bis-phenol A terminated. Moreover, it is believed that halomethylated groups on phenolic-terminated polymers may be particularly reactive to subsequent crosslinking or chain extension. In contrast, it is generally believed that halomethylation does not take place on the terminal aromatic groups with electron withdrawing substituents, such as benzophenone, halogenated benzophenone, or the like. The "A" group terminated materials may also function as an adhesive, and in applications such as thermal ink jet printheads, the use of the crosslinked "A" group terminated polymer may reduce or eliminate the need for an epoxy adhesive to bond the heater plate to the channel plate.

The photopatternable polymer can be cured by uniform exposure to actinic radiation at wavelengths and/or energy levels capable of causing crosslinking or chain extension of the polymer through the photosensitivity-imparting groups. Alternatively, the photopatternable polymer is developed by imagewise exposure of the material to radiation at a wavelength and/or at an energy level to which the photosensitivity-imparting groups are sensitive. Typically, a photoresist composition will contain the photopatternable polymer, an optional solvent for the photopatternable polymer, an optional sensitizer, and an optional photoinitiator. Solvents may be particularly desirable when the uncrosslinked photopatternable polymer has a high T_g. The solvent and photopatternable polymer typically are present in relative amounts of from 0 to about 99 percent by weight solvent and from about 1 to 100 percent polymer, preferably are present in relative amounts of from about 20 to about 60 percent by weight solvent and from about 40 to about 80 percent by weight polymer, and more preferably are present in relative amounts of from about 30 to about 60 percent by weight solvent and from about 40 to about 70 percent by weight polymer, although the relative amounts can be outside these ranges.

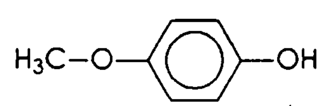
Sensitizers absorb light energy and facilitate the transfer of energy to unsaturated bonds which can then react to crosslink or chain extend the resin. Sensitizers frequently expand the useful energy wavelength range for photoexposure, and typically are aromatic light absorbing chromophores. Sensitizers can also lead to the formation of photoinitiators, which can be free radical or ionic. When present, the optional sensitizer and the photopatternable polymer typically are present in relative amounts of from about 0.1 to about 20 percent by weight sensitizer and from about 80 to about 99.9 percent by weight photopatternable polymer, and preferably are present in relative amounts of from about 1 to about 10 percent by weight sensitizer and from about 90 to about 99 percent by weight photopatternable polymer, although the relative amounts can be outside these ranges.

Photoinitiators generally generate ions or free radicals which initiate polymerization upon exposure to actinic radiation. When present, the optional photoinitiator and the photopatternable polymer typically are present in relative amounts of from about 0.1 to about 20 percent by weight photoinitiator and from about 80 to about 99.9 percent by weight photopatternable polymer, and preferably are present in relative amounts of from about 1 to about 10 percent by weight photoinitiator and from about 90 to about 99 percent by weight photopatternable polymer, although the relative amounts can be outside these ranges.

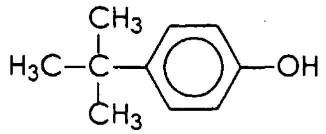
A single material can also function as both a sensitizer and a photoinitiator.

Examples of specific sensitizers and photoinitiators include Michler's ketone (Aldrich Chemical Co.), Darocure 1173, Darocure 4265, Irgacure 184, Irgacure 261, and Irgacure 907 (available from Ciba-Geigy, Ardsley, New York), and mixtures thereof. Further background material on initiators is disclosed in, for example, Ober et al., *J.M.S. - Pure Appl. Chem.*, **A30** (12), 877-897 (1993); G. E. Green, B. P. Stark, and S. A. Zahir, "Photocrosslinkable Resin Systems, " *J. Macro. Sci. -- Revs. Macro. Chem.*, C21(2), 187 (1981); H. F. Gruber, "Photoinitiators for Free Radical Polymerization," *Prog. Polym. Sci.*, Vol. 17, 953 (1992); Johann G. Kloosterboer, "Network Formation by Chain Crosslinking Photopolymerization and Its Applications in Electronics," *Advances in Polymer Science*, ***89***, Springer-Verlag Berlin Heidelberg (1988); and "Diaryliodonium Salts as Thermal Initiators of Cationic Polymerization," J. V. Crivello, T.P. Lockhart, and J. L. Lee, *J. of Polymer Science: Polymer Chemistry Edition*, ***21***, 97 (1983). Sensitizers are available from, for example, Aldrich Chemical Co., Milwaukee, WI, and Pfaltz and Bauer, Waterberry, CT. Benzophenone and its derivatives can function as photosensitizers. Triphenylsulfonium and diphenyl iodonium salts are examples of typical cationic photoinitiators.

Inhibitors may also optionally be present in the photoresist containing the photopatternable polymer. Examples of suitable inhibitors include MEHQ, a methyl ether of hydroquinone, of the formula



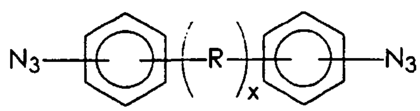
t-butylcatechol, of the formula



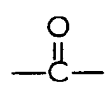
hydroquinone, of the formula

and the like, the inhibitor typically present in an amount of from about 500 to about 1,500 parts per million by weight of a photoresist solution containing about 40 percent by weight polymer solids, although the amount can be outside this range.

One specific example of a class of suitable sensitizers or initiators is that of bis(azides), of the general formula

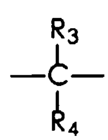


wherein R is



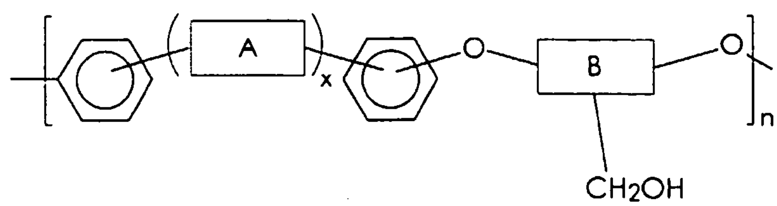
$-R_1C{=}CR_2-$,

or

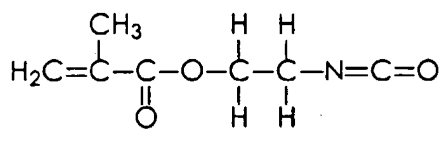


wherein R_1, R_2, R_3, and R_4 each, independently of the others, is a hydrogen atom, an alkyl group, including saturated, unsaturated, and cyclic alkyl groups, preferably with from 1 to about 30 carbon atoms, and more preferably with from 1 to about 6 carbon atoms, a substituted alkyl group, an aryl group, preferably with from 6 to about 18 carbon atoms, and more preferably with about 6 carbon atoms, a substituted aryl group, an arylalkyl group, preferably with from 7 to about 48 carbon atoms, and more preferably with from about 7 to about 8 carbon atoms, or a substituted arylalkyl group, and x is 0 or 1.

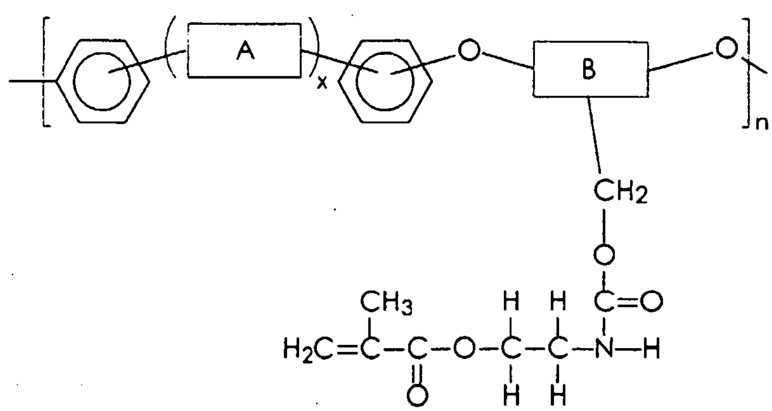
A hydroxyalkylated polymer can be further reacted to render it more photosensitive. For example, a hydroxymethylated polymer of the formula



can react with isocyanato-ethyl methacrylate, of the formula



(available from Polysciences, Warrington, PA) to form a photoactive polymer of the formula

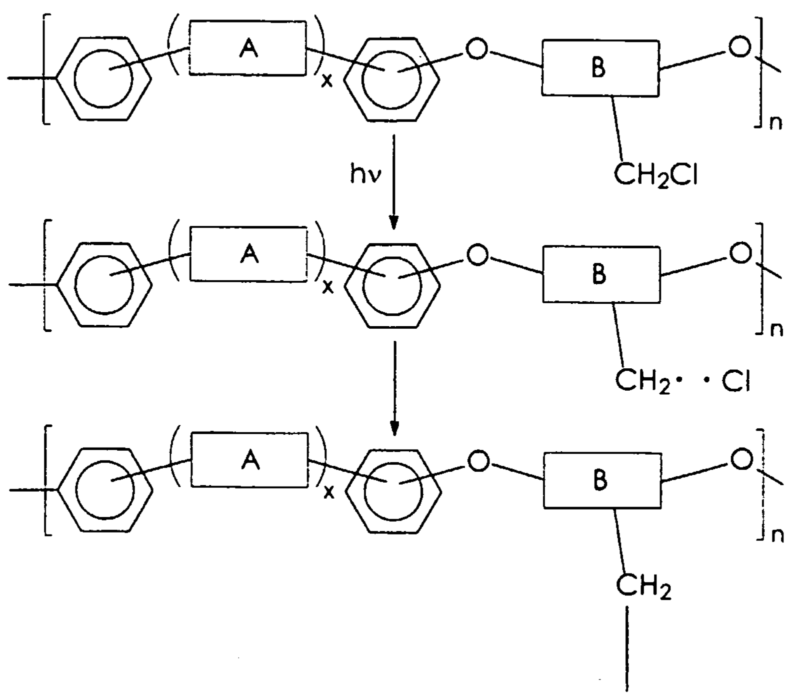


This reaction can be carried out in methylene chloride at 25°C with 1 part by weight polymer, 1 part by weight isocyanatoethyl methacrylate, and 50 parts by weight methylene chloride. Typical reaction temperatures are from about 0 to about 50°C, with 10 to 25°C preferred. Typical reaction times are between about 1 and about 24 hours, with about 16 hours preferred. During exposure to, for example, ultraviolet radiation, the ethylenic bond opens and crosslinking or chain extension occurs at that site.

Alternatively, the haloalkylated polymer can be patterned with electron beam, ultraviolet, or x-ray radiation. Typical suitable wavelengths for ultraviolet radiation are from about 200 to about 365 nanometers, and preferably deep uv radiation of from about 200 to about 260 nanometers, although the wavelength can be outside this range. Typical suitable energy levels for e-beam radiation are from about 600 to about 2,000 megarads, and preferably about 1,000 megarads, although the energy level can be outside this range. Typical suitable x-ray radiation levels are from about 100 to about 2,500 milliJoules per square centimeter, or from about 600 to about 2,000 rads, although the radiation levels can be outside these ranges. Suitable imaging apparatus for e-beam exposure includes Van de Graaf generators and other high energy particle accelerators, such as those available from Energy Science, Woburn MA, Radionics, Woburn, MA, scanning electron microscope equipment, such as that available from Siemens AG, and the like. Other suitable e-beam sources include 20 KV exposures using a LaB_6 electron gun at 0.24 megarads per hour, and an RCA Transmission Electron Microscope Model 3G modified to provide a source between 22 and 44 KeV electrons. Suitable imaging apparatus for ultraviolet exposure includes equipment available from Adcotech Corp., Advance Process Supply Co., Argus International, Arthur Blank & Co., Inc., Chemcut Corp., Chemical Etching Equipment & Supply Co., The Christopher Group, Cirplex/Quality Assurance Marketing Div., Colight, Inc., DGE, Inc., Dyna/Pert, Div. of Emhart Corp., Dyonics Inc., Industrial Div., Fusion Systems Corp., Gyrex Corp., subsidiary of Allied Chemical Co., Hybrid Technology Group, Inc., International Printing Machines Corp., Geo. Koch & Sons, Ashdee Div., Kras Corp., Machine Technology,

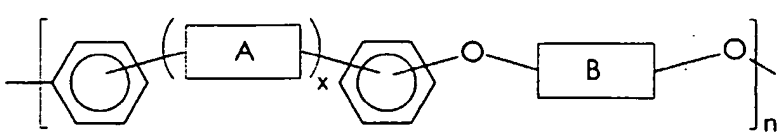
Inc., Magnum Technology Inc., Nationwide Circuit Products, Stenning Instruments Inc., UV Process Supply, Inc., Uvexs, Inc., UVP, Inc., Ultraviolet Products, Xenon Corp., and the like. Any source of x-ray radiation can be used for x-ray imaging apparatus. Further information regarding suitable exposure apparatus is disclosed in, for example, *Reactive Cure Systems: UV-IR-EB,* CAPTAN Associates Inc., PO Box 504, Brick, NJ (1994), and in "Fundamental Aspects of Electron Beam Lithography," G. M. Venkatesh et al., *Polymer Preprints,* 22(2), 335 (1981).

While not being limited to any particular theory, it is believed that exposure to, for example, e-beam, ultraviolet, or x-ray radiation generally results in free radical cleavage of the halogen atom from the methyl group to form a benzyl radical. Crosslinking or chain extension then occurs at the "long" bond sites, as illustrated below for the chloromethylated polymer:

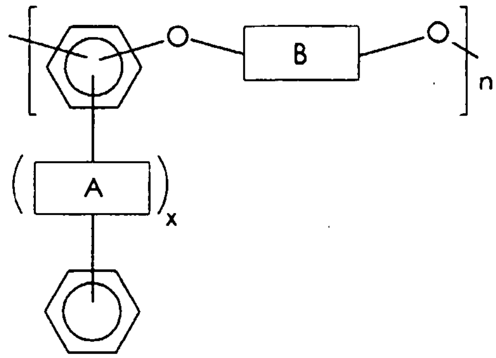


Many of the photosensitivity-imparting groups which are indicated above as being capable of enabling crosslinking or chain extension of the polymer upon exposure to actinic radiation can also enable crosslinking or chain extension of the polymer upon exposure to elevated temperatures; thus the polymers of the present invention can also, if desired, be used in applications wherein thermal curing is employed.

In all of the above reactions and substitutions illustrated above for the polymer of the formula

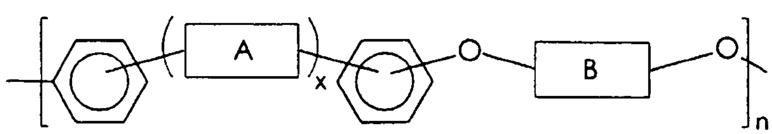


it is to be understood that analogous reactions and substitutions will occur for the polymer of the formula

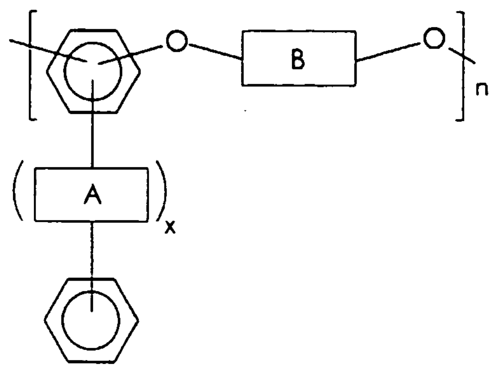


In another preferred embodiment of the present invention, a photoresist is prepared which comprises a mixture of the polymer substituted with photoactive groups and the halomethylated polymer. The halomethylated polymer, which can be used as an intermediate in the synthesis of the photosensitivity-imparting group substituted polymer, also functions as an accelerator which generates free radicals upon exposure to ultraviolet light, and thus can be used instead of or in addition to other accelerators or sensitizers, such as Michler's ketone or the like. In addition, the substitution of the halomethylated precursor with the photosensitivity-imparting groups can be controlled so as to yield a mixture containing a known proportion of the halomethyl residue. Accordingly, a photoresist can be prepared of the photosensitivity-imparting group substituted polymer without the need to add an additional initiator to the precursor material. Typically, the halomethylated polymer (which typically is substituted to a degree of from about 0.25 to about 2.0 halomethyl groups per monomer repeat unit, preferably from about 1 to about 2 halomethyl groups per monomer repeat unit, and more preferably from about 1.5 to about 2 halomethyl groups per monomer repeat unit) and the photosensitivity-imparting group substituted polymer (which typically is substituted to a degree of from about 0.25 to about 2.0 photosensitivity-imparting groups per monomer repeat unit, preferably from about 0.5 to about 1 photosensitivity-imparting group per monomer repeat unit, and more preferably from about 0.7 to about 0.8 photosensitivity-imparting group per monomer repeat unit) are present in relative amounts such that the degree of substitution when measured for the blended composition is from about 0.25 to about 1.5, preferably from about 0.5 to about 0.8, and more preferably about 0.75 photosensitivity-imparting groups per monomer repeat unit, and from about 0.25 to about 2.25, preferably from about 0.75 to about 2, and more preferably from about 0.75 to about 1 halomethyl group per monomer repeat unit, although the relative amounts can be outside these ranges. Similarly, a polymer substituted with both halomethyl and photosensitivity-imparting groups can function as an accelerator. In this instance, the accelerating polymer typically exhibits a degree of substitution of from about 0.25 to about 1.5, preferably from about 0.5 to about 0.8, and more preferably about 0.75 photosensitivity-imparting groups per monomer repeat unit, and from about 0.25 to about 2.25, preferably from about 0.75 to about 2, and more preferably from about 0.75 to about 1 halomethyl group per monomer repeat unit, although the relative amounts can be outside these ranges.

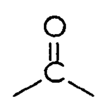
Particularly preferred as reaction accelerators are polymers of the formula

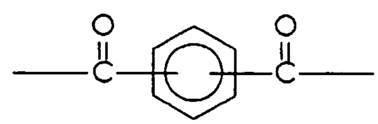


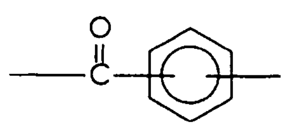
or



wherein A is selected so that the monomeric unit contains a benzophenone moiety and x and B are as defined hereinabove, said polymer having at least one halomethyl substituent per monomer repeat unit in at least some of the monomer repeat units of the polymer, said polymer having at least one photosensitivity-imparting group per monomer repeat unit in at least some of the monomer repeat units of the polymer. Examples of suitable A groups for this embodiment include







and the like. While not being limited to any particular theory, it is believed that in this embodiment, the presence of the benzophenone moiety acts as a photoabsorbing element in the polymer backbone and contributes to the photoinitiating characteristics of the polymer. In this embodiment, advantages include high sensitivity, high developability, and high aspect ratios in thick films.

When the halomethylated polymer is present in relatively high concentrations in a photoresist with respect to the amount of photosensitivity-imparting group substituted polymer, the halomethylated material can also act as an ultraviolet polymerization inhibitor.

Photopatternable polymers prepared by the process of the present invention can be used as components in ink jet printheads. The printheads of the present invention can be of any suitable configuration. An example of a suitable configuration, suitable in this instance for thermal ink jet printing, is illustrated schematically in Figure 1, which depicts an enlarged, schematic isometric view of the front face 29 of a printhead 10 showing the array of droplet emitting nozzles 27. Referring also to Figure 2, discussed later, the lower electrically insulating substrate or heating element plate 28 has the heating elements 34 and addressing electrodes 33 patterned on surface 30 thereof, while the upper substrate or channel plate 31 has parallel grooves 20 which extend in one direction and penetrate through the upper substrate front face edge 29. The other end of grooves 20 terminate at slanted wall 21, the floor 41 of the internal recess 24 which is used as the ink supply manifold for the capillary filled ink channels 20, has an opening 25 therethrough for use as an ink fill hole. The surface of the channel plate with the grooves are aligned and bonded to the

heater plate 28, so that a respective one of the plurality of heating elements 34 is positioned in each channel, formed by the grooves and the lower substrate or heater plate. Ink enters the manifold formed by the recess 24 and the lower substrate 28 through the fill hole 25 and by capillary action, fills the channels 20 by flowing through an elongated recess 38 formed in the thick film insulative layer 18. The ink at each nozzle forms a meniscus, the surface tension of which prevents the ink from weeping therefrom. The addressing electrodes 33 on the lower substrate or channel plate 28 terminate at terminals 32. The upper substrate or channel plate 31 is smaller than that of the lower substrate in order that the electrode terminals 32 are exposed and available for wire bonding to the electrodes on the daughter board 19, on which the printhead 10 is permanently mounted. Layer 18 is a thick film passivation layer, discussed later, sandwiched between the upper and lower substrates. This layer is etched to expose the heating elements, thus placing them in a pit, and is etched to form the elongated recess to enable ink flow between the manifold 24 and the ink channels 20. In addition, the thick film insulative layer is etched to expose the electrode terminals.

A cross sectional view of Figure 1 is taken along view line 2-2 through one channel and shown as Figure 2 to show how the ink flows from the manifold 24 and around the end 21 of the groove 20 as depicted by arrow 23. As is disclosed in U.S. Patent 4,638,337, U.S. Patent 4,601,777, and U.S. Patent Re. 32,572, a plurality of sets of bubble generating heating elements 34 and their addressing electrodes 33 can be patterned on the polished surface of a single side polished (100) silicon wafer. Prior to patterning, the multiple sets of printhead electrodes 33, the resistive material that serves as the heating elements 34, and the common return 35, the polished surface of the wafer is coated with an underglaze layer 39 such as silicon dioxide, having a typical thickness of from about 500nm (5,000 Angstroms) to about 2 micrometers (microns), although the thickness can be outside this range. The resistive material can be a doped polycrystalline silicon, which can be deposited by chemical vapor deposition (CVD) or any other well known resistive material such as zirconium boride (ZrB_2). The common return and the addressing electrodes are typically aluminum leads deposited on the underglaze and over the edges of the heating elements. The common return ends or terminals 37 and addressing electrode terminals 32 are positioned at predetermined locations to allow clearance for wire bonding to the electrodes (not shown) of the daughter board 19, after the channel plate 31 is attached to make a printhead. The common return 35 and the addressing electrodes 33 are deposited to a thickness typically of from about 0.5 to about 3 micrometers (microns), although the thickness can be outside this range, with the preferred thickness being 1.5 micrometers (microns).

If polysilicon heating elements are used, they may be subsequently oxidized in steam or oxygen at a relatively high temperature, typically about 1,100°C although the temperature can be above or below this value, for a period of time typically of from about 50 to about 80 minutes, although the time period can be outside this range, prior to the deposition of the aluminum leads, in order to convert a small portion of the polysilicon to SiO_2. In such cases, the heating elements are thermally oxidized to achieve an overglaze (not shown) of SiO_2 with a thickness typically of from about 50nm (500 Angstroms) to about 1 micrometer (micron), although the thickness can be outside this range, which has good integrity with substantially no pinholes.

In one embodiment, polysilicon heating elements are used and an optional silicon dioxide thermal oxide layer 17 is grown from the polysilicon in high temperature steam. The thermal oxide layer is typically grown to a thickness of from about 0.5 to about 1 micron, although the thickness can be outside this range, to protect and insulate the heating elements from the conductive ink. The thermal oxide is removed at the edges of the polysilicon heating elements for attachment of the addressing electrodes and common return, which are then patterned and deposited. If a resistive material such as zirconium boride is used for the heating elements, then other suitable well known insulative materials can be used for the protective layer thereover. Before electrode passivation, a tantalum (Ta) layer (not shown) can be optionally deposited, typically to a thickness of about 1 micron, although the thickness can be above or below this value, on the heating element protective layer 17 for added protection thereof against the cavitational forces generated by the collapsing ink vapor bubbles during printhead operation. The tantalum layer is etched off all but the protective layer 17 directly over the heating elements using, for example, CF_4/O_2 plasma etching. For polysilicon heating elements, the aluminum common return and addressing electrodes typically are deposited on the underglaze layer and over the opposing edges of the polysilicon heating elements which have been cleared of oxide for the attachment of the common return and electrodes.

For electrode passivation, a film 16 is deposited over the entire wafer surface, including the plurality of sets of heating elements and addressing electrodes. The passivation film 16 provides an ion barrier which will protect the exposed electrodes from the ink. Examples of suitable ion barrier materials for passivation film 16 include polyimide, plasma nitride, phosphorous doped silicon dioxide, materials disclosed herein as being suitable for insulative layer 18, and the like, as well as any combinations thereof. An effective ion barrier layer is generally achieved when its thickness is from about 100nm (1000 Angstroms) to about 10 micrometers (microns), although the thickness can be outside this range. In 300 dpi printheads, passivation layer 16 preferably has a thickness of about 3 micrometers (microns), although the thickness can be above or below this value. In 600 dpi printheads, the thickness of passivation layer 16 preferably is such that the combined thickness of layer 16 and layer 18 is about 25 micrometers (microns), although the thickness can be above or below this value. The passivation film or layer 16 is etched off of the terminal ends of the common

return and addressing electrodes for wire bonding later with the daughter board electrodes. This etching of the silicon dioxide film can be by either the wet or dry etching method. Alternatively, the electrode passivation can be by plasma deposited silicon nitride (Si_3N_4).

Next, a thick film type insulative layer 18, of a polymeric material discussed in further detail herein, is formed on the passivation layer 16, typically having a thickness of from about 10 to about 100 micrometers (microns) and preferably in the range of from about 25 to about 50 micrometers (microns), although the thickness can be outside these ranges. Even more preferably, in 300 dpi printheads, layer 18 preferably has a thickness of about 30 micrometers (microns), and in 600 dpi printheads, layer 18 preferably has a thickness of from about 20 to about 22 micrometers (microns), although other thicknesses can be employed. The insulative layer 18 is photolithographically processed to enable etching and removal of those portions of the layer 18 over each heating element (forming recesses 26), the elongated recess 38 for providing ink passage from the manifold 24 to the ink channels 20, and over each electrode terminal 32, 37. The elongated recess 38 is formed by the removal of this portion of the thick film layer 18. Thus, the passivation layer 16 alone protects the electrodes 33 from exposure to the ink in this elongated recess 38. Optionally, if desired, insulative layer 18 can be applied as a series of thin layers of either similar or different composition. Typically, a thin layer is deposited, photoexposed, partially cured, followed by deposition of the next thin layer, photoexposure, partial curing, and the like. The thin layers constituting thick film insulative layer 18 contain a polymer of the formula indicated hereinabove. In one embodiment of the present invention, a first thin layer is applied to contact layer 16, said first thin layer containing a mixture of a polymer of the formula indicated hereinabove and an epoxy polymer, followed by photoexposure, partial curing, and subsequent application of one or more successive thin layers containing a polymer of the formula indicated hereinabove.

Figure 3 is a similar view to that of Figure 2 with a shallow anisotropically etched groove 40 in the heater plate, which is silicon, prior to formation of the underglaze 39 and patterning of the heating elements 34, electrodes 33 and common return 35. This recess 40 permits the use of only the thick film insulative layer 18 and eliminates the need for the usual electrode passivating layer 16. Since the thick film layer 18 is impervious to water and relatively thick (typically from about 20 to about 40 microns, although the thickness can be outside this range), contamination introduced into the circuitry will be much less than with only the relatively thin passivation layer 16 well known in the art. The heater plate is a fairly hostile environment for integrated circuits. Commercial ink generally entails a low attention to purity. As a result, the active part of the heater plate will be at elevated temperature adjacent to a contaminated aqueous ink solution which undoubtedly abounds with mobile ions. In addition, it is generally desirable to run the heater plate at a voltage of from about 30 to about 50 volts, so that there will be a substantial field present. Thus, the thick film insulative layer 18 provides improved protection for the active devices and provides improved protection, resulting in longer operating lifetime for the heater plate.

When a plurality of lower substrates 28 are produced from a single silicon wafer, at a convenient point after the underglaze is deposited, at least two alignment markings (not shown) preferably are photolithographically produced at predetermined locations on the lower substrates 28 which make up the silicon wafer. These alignment markings are used for alignment of the plurality of upper substrates 31 containing the ink channels. The surface of the single sided wafer containing the plurality of sets of heating elements is bonded to the surface of the wafer containing the plurality of ink channel containing upper substrates subsequent to alignment.

As disclosed in U.S. Patent 4,601,777 and U.S. Patent 4,638,337, the channel plate is formed from a two side polished, (100) silicon wafer to produce a plurality of upper substrates 31 for the printhead. After the wafer is chemically cleaned, a pyrolytic CVD silicon nitride layer (not shown) is deposited on both sides. Using conventional photolithography, a via for fill hole 25 for each of the plurality of channel plates 31 and at least two vias for alignment openings (not shown) at predetermined locations are printed on one wafer side. The silicon nitride is plasma etched off of the patterned vias representing the fill holes and alignment openings. A potassium hydroxide (KOH) anisotropic etch can be used to etch the fill holes and alignment openings. In this case, the [111] planes of the (100) wafer typically make an angle of about 54.7 degrees with the surface of the wafer. The fill holes are small square surface patterns, generally of about 20 mils (500 microns) per side, although the dimensions can be above or below this value, and the alignment openings are from about 60 to about 80 mils (1.5 to 3 millimeters) square, although the dimensions can be outside this range. Thus, the alignment openings are etched entirely through the 20 mil (0.5 millimeter) thick wafer, while the fill holes are etched to a terminating apex at about halfway through to three-quarters through the wafer. The relatively small square fill hole is invariant to further size increase with continued etching so that the etching of the alignment openings and fill holes are not significantly time constrained.

Next, the opposite side of the wafer is photolithographically patterned, using the previously etched alignment holes as a reference to form the relatively large rectangular recesses 24 and sets of elongated, parallel channel recesses that will eventually become the ink manifolds and channels of the printheads. The surface 22 of the wafer containing the manifold and channel recesses are portions of the original wafer surface (covered by a silicon nitride layer) on which an adhesive, such as a thermosetting epoxy, will be applied later for bonding it to the substrate containing the plurality of sets of heating elements. The adhesive is applied in a manner such that it does not run or spread into the

grooves or other recesses. The alignment markings can be used with, for example, a vacuum chuck mask aligner to align the channel wafer on the heating element and addressing electrode wafer. The two wafers are accurately mated and can be tacked together by partial curing of the adhesive. Alternatively, the heating element and channel wafers can be given precisely diced edges and then manually or automatically aligned in a precision jig. Alignment can also be performed with an infrared aligner-bonder, with an infrared microscope using infrared opaque markings on each wafer to be aligned, or the like. The two wafers can then be cured in an oven or laminator to bond them together permanently. The channel wafer can then be milled to produce individual upper substrates. A final dicing cut, which produces end face 29, opens one end of the elongated groove 20 producing nozzles 27. The other ends of the channel groove 20 remain closed by end 21. However, the alignment and bonding of the channel plate to the heater plate places the ends 21 of channels 20 directly over elongated recess 38 in the thick film insulative layer 18 as shown in Figure 2 or directly above the recess 40 as shown in Figure 3 enabling the flow of ink into the channels from the manifold as depicted by arrows 23. The plurality of individual printheads produced by the final dicing are bonded to the daughter board and the printhead electrode terminals are wire bonded to the daughter board electrodes.

In one embodiment, a heater wafer with a phosphosilicate glass layer is spin coated with a solution of Z6020 adhesion promoter (0.01 weight percent in 95 parts methanol and 5 parts water, Dow Corning) at 3000 revolutions per minute for 10 seconds and dried at 100°C for between 2 and 10 minutes. The wafer is then allowed to cool at 25°C for 5 minutes before spin coating the photoresist containing the photopatternable polymer onto the wafer at between 1,000 and 3,000 revolutions per minute for between 30 and 60 seconds. The photoresist solution is made by dissolving polyarylene ether ketone with 0.75 acryloyl groups and 0.75 chloromethyl groups per repeat unit and a weight average molecular weight of 25,000 in N-methylpyrrolidinone at 40 weight percent solids with Michler's ketone (1.2 parts ketone per every 10 parts of 40 weight percent solids polymer solution). The film is heated (soft baked) in an oven for between 10 and 15 minutes at 70°C. After cooling to 25°C over 5 minutes, the film is covered with a mask and exposed to 365 nanometer ultraviolet light, amounting to between 150 and 1,500 milliJoules per cm^2. The exposed wafer is then heated at 70°C for 2 minutes post exposure bake, followed by cooling to 25°C over 5 minutes. The film is developed with 60:40 chloroform/cyclohexanone developer, washed with 90:10 hexanes/cyclohexanone, and then dried at 70°C for 2 minutes. A second developer/wash cycle is carried out if necessary to obtain a wafer with clean features. The processed wafer is transferred to an oven at 25°C, and the oven temperature is raised from 25 to 90°C at 2°C per minute. The temperature is maintained at 90°C for 2 hours, and then increased to 260°C at 2°C per minute. The oven temperature is maintained at 260°C for 2 hours and then the oven is turned off and the temperature is allowed to cool gradually to 25°C. When thermal cure of the photoresist films is carried out under inert atmosphere, such as nitrogen or one of the noble gases, such as argon, neon, krypton, xenon, or the like, there is markedly reduced oxidation of the developed film and improved thermal and hydrolytic stability of the resultant devices. Moreover, adhesion of developed photoresist film is improved to the underlying substrate. If a second layer is spin coated over the first layer, the heat cure of the first developed layer can be stopped between 80 and 260°C before the second layer is spin coated onto the first layer. A second thicker layer is deposited by repeating the above procedure a second time. This process is intended to be a guide in that procedures can be outside the specified conditions depending on film thickness and photoresist molecular weight. Films at 30 micrometers (microns) have been developed with clean features at 600 dots per inch.

In another instance, the spin coated film of the first layer is prepared as described above using a photoresist solution of chloromethylated polyarylene ether ketone (1.5 chloromethyl groups per polymer repeat unit) as a 40 weight percent solids solution in N-methylpyrrolidinone. The film is exposed to an ultra violet laser beam which tracks a preprogrammed pattern, heated at 70°C for 2 minutes post exposure bake, followed by cooling to 25°C over 5 minutes. The film is developed with 1:1 chloroform/cyclohexanone developer, washed with 9:1 hexanes/cyclohexanone, and then dried at 70°C for 2 minutes. The processed wafer has well resolved features of crosslinked chloromethylated polyarylene ether ketone where the laser beam contacted the film.

For best results with respect to well-resolved features and high aspect ratios, photoresist compositions of the present invention are free of particulates prior to coating onto substrates. In one preferred embodiment, the photoresist composition containing the photopatternable polymer is subjected to filtration through a 2 micron nylon filter cloth (available from Tetko). The photoresist solution is filtered through the cloth under yellow light or in the dark as a solution containing from about 30 to about 60 percent by weight solids using compressed air (up to about 60 psi) and a pressure filtration funnel. No dilution of the photoresist solution is required, and concentrations of an inhibitor (such as, for example, MEHQ) can be as low as, for example, 500 parts per million or less by weight without affecting shelf life. No build in molecular weight of the photopatternable polymer is observed during this filtration process. While not being limited to any particular theory, it is believed that in some instances, such as those when unsaturated ester groups are present on the photopolymerizable polymer, compressed air yields results superior to those obtainable with inert atmosphere because oxygen in the compressed air acts as an effective inhibitor for the free radical polymerization of unsaturated ester groups such as acrylates and methacrylates.

In a particularly preferred embodiment, the photopatternable polymer is admixed with an epoxy resin in relative amounts of from about 75 parts by weight photopatternable polymer and about 25 parts by weight epoxy resin to about

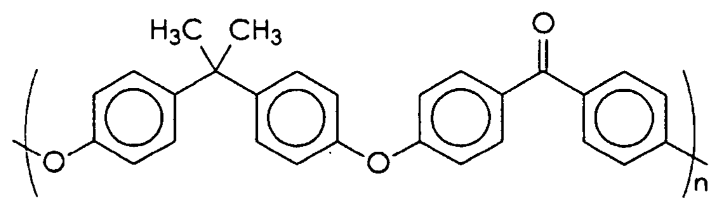
90 parts by weight photopatternable polymer and about 10 parts by weight epoxy resin.

The present invention also encompasses printing processes with printheads according to the present invention. One embodiment of the present invention is directed to an ink jet printing process which comprises (1) preparing an ink jet printhead comprising a plurality of channels, wherein the channels are capable of being filled with ink from an ink supply and wherein the channels terminate in nozzles on one surface of the printhead, said preparation being according to the process of the present invention; (2) filling the channels with an ink; and (3) causing droplets of ink to be expelled from the nozzles onto a receiver sheet in an image pattern. A specific embodiment of this process is directed to a thermal ink jet printing process, wherein the droplets of ink are caused to be expelled from the nozzles by heating selected channels in an image pattern. The droplets can be expelled onto any suitable receiver sheet, such as fabric, plain paper such as Xerox® 4024 or 4010, coated papers, or transparency materials.

All parts and percentages in the Examples are by weight unless otherwise indicated.

EXAMPLE I

A polyarylene ether ketone of the formula



wherein n is between about 2 and about 30 (hereinafter referred to as poly(4-CPK-BPA)) was prepared as follows. A 5 liter, 3-neck round-bottom flask equipped with a Dean-Stark (Barrett) trap, condenser, mechanical stirrer, argon inlet, and stopper was situated in a silicone oil bath. 4,4'-Dichlorobenzophenone (Aldrich 11,370, Aldrich Chemical Co., Milwaukee, WI, 250 grams), bis-phenol A (Aldrich 23,965-8, 244.8 grams), potassium carbonate (327.8 grams), anhydrous *N,N*-dimethylacetamide (1,500 milliliters), and toluene (275 milliliters) were added to the flask and heated to 175°C (oil bath temperature) while the volatile toluene component was collected and removed. After 48 hours of heating at 175°C with continuous stirring, the reaction mixture was filtered to remove insoluble salts, and the resultant solution was added to methanol (5 gallons) to precipitate the polymer. The polymer was isolated by filtration, and the wet filter cake was washed with water (3 gallons) and then with methanol (3 gallons). The yield was 360 grams of vacuum dried product. The molecular weight of the polymer was determined by gel permeation chromatography (gpc) (elution solvent was tetrahydrofuran) with the following results: M_n 3,601, M_{peak} 5,377, M_w 4,311, M_z 8,702, and M_{z+1} 12,951. The glass transition temperature of the polymer was between 125 and 155°C as determined using differential scanning calorimetry at a heating rate of 20°C per minute dependent on molecular weight. Solution cast films from methylene chloride were clear, tough, and flexible. As a result of the stoichiometries used in the reaction, it is believed that this polymer had end groups derived from bis-phenol A.

A solution of chloromethyl ether in methyl acetate was made by adding 282.68 grams (256 milliliters) of acetyl chloride to a mixture of dimethoxy methane (313.6 grams, 366.8 milliliters) and methanol (10 milliliters) in a 5 liter 3-neck round-bottom flask equipped with a mechanical stirrer, argon inlet, reflux condenser, and addition funnel. The solution was diluted with 1,066.8 milliliters of 1,1,2,2-tetrachloroethane and then tin tetrachloride (2.4 milliliters) was added via a gas-tight syringe along with 1,1,2,2-tetrachloroethane (133.2 milliliters) using an addition funnel. The reaction solution was heated to 500°C. Thereafter, a solution of poly(4-CPK-BPA) prepared as described above (160.8 grams) in 1,000 milliliters of tetrachloroethane was added rapidly. The reaction mixture was then heated to reflux with an oil bath set at 110°C. After four hours reflux with continuous stirring, heating was discontinued and the mixture was allowed to cool to 25°C. The reaction mixture was transferred in stages to a 2 liter round bottom flask and concentrated using a rotary evaporator with gentle heating up to 50°C while reduced pressure was maintained with a vacuum pump trapped with liquid nitrogen. The concentrate was added to methanol (4 gallons) to precipitate the polymer using a Waring blender. The polymer was isolated by filtration and vacuum dried to yield 200 grams of poly(4-CPK-BPA) with 1.5 chloromethyl groups per repeat unit as identified using ^{1}H NMR spectroscopy. When the same reaction was carried out for 1, 2, 3, and 4 hours, the amount of chloromethyl groups per repeat unit was 0.76, 1.09, 1.294, and 1.496, respectively.

Solvent free polymer was obtained by reprecipitation of the polymer (75 grams) in methylene chloride (500 grams) into methanol (3 gallons) followed by filtration and vacuum drying to yield 70.5 grams (99.6% theoretical yield) of solvent free polymer.

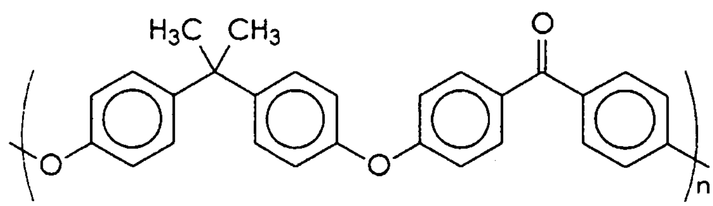
When the reaction was carried out under similar conditions except that 80.4 grams of poly(4-CPK-BPA) was used instead of 160.8 grams and the amounts of the other reagents were the same as indicated above, the polymer is formed with 1.31, 1.50, 1.75, and 2 chloromethyl groups per repeat unit in 1, 2, 3, and 4 hours, respectively, at 110°C (oil bath temperature).

When 241.2 grams of poly(4-CPK-BPA) was used instead of 160.8 grams with the other reagents fixed, poly(CPK-BPA) was formed with 0.79, 0. 90, 0.98, 1.06, 1.22, and 1.38 chloromethyl groups per repeat unit in 1, 2, 3, 4, 5, and 6 hours, respectively, at 110°C (oil bath temperature).

When 321.6 grams of poly(4-CPK-BPA) was used instead of 160.8 grams with the other reagents fixed, poly(CPK-BPA) was formed with 0.53, 0.59, 0.64, 0.67, 0.77, 0.86, 0.90, and 0.97 chloromethyl groups per repeat unit in 1, 2, 3, 4, 5, 6, 7, and 8 hours, respectively, at 110°C (oil bath temperature).

EXAMPLE II

A polyarylene ether ketone of the formula

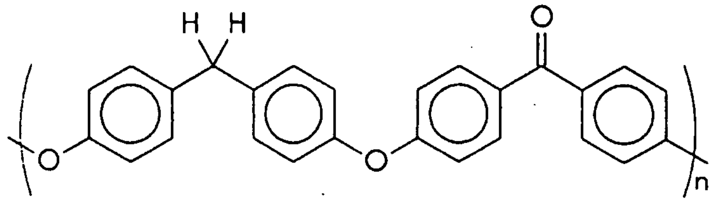


wherein n is between about 6 and about 30 (hereinafter referred to as poly(4-CPK-BPA)) was prepared as follows. A 1 liter, 3-neck round-bottom flask equipped with a Dean-Stark (Barrett) trap, condenser, mechanical stirrer, argon inlet, and stopper was situated in a silicone oil bath. 4,4'-Dichlorobenzophenone (Aldrich 11,370, Aldrich Chemical Co., Milwaukee, WI, 50 grams), bis-phenol A (Aldrich 23,965-8, 48.96 grams), potassium carbonate (65.56 grams), anhydrous *N,N*-dimethylacetamide (300 milliliters), and toluene (55 milliliters) were added to the flask and heated to 175°C (oil bath temperature) while the volatile toluene component was collected and removed. After 24 hours of heating at 175°C with continuous stirring, an aliquot of the reaction product that had been precipitated into methanol was analyzed by gel permeation chromatography (gpc) (elution solvent was tetrahydrofuran) with the following results: M_n 4464, M_{peak} 7583, M_w 7927, M_z 12,331, and M_{z+1} 16,980. After 48 hours at 175°C with continuous stirring, the reaction mixture was filtered to remove potassium carbonate and precipitated into methanol (2 gallons). The polymer (poly (4-CPK-BPA)) was isolated in 86% yield after filtration and drying *in vacuo*. GPC analysis was as follows: M_n 5347, M_{peak} 16,126, M_w 15,596, M_z 29,209, and M_{z+1} 42,710. The glass transition temperature of the polymer was about 120±10°C as determined using differential scanning calorimetry at a heating rate of 20°C per minute. Solution cast films from methylene chloride were clear, tough, and flexible. As a result of the stoichiometries used in the reaction, it is believed that this polymer had end groups derived from bis-phenol A.

The resulting polyarylene ether ketone was chloromethylated by the following procedure. A solution of chloromethyl ether in methyl acetate was made by adding 35.3 grams of acetyl chloride to a mixture of dimethoxy methane (45 milliliters) and methanol (1.25 milliliters) in a 500 milliliter 3-neck round-bottom flask equipped with a mechanical stirrer, argon inlet, reflux condenser, and addition funnel. The solution was diluted with 150 milliliters of 1,1,2,2-tetrachloroethane and then tin tetrachloride (0.3 milliliters) was added via syringe. The solution was heated to reflux with an oil bath set at 110°C. Thereafter, a solution of poly(4-CPK-BPA) (10 grams) in 125 milliliters of 1,1,2,2-tetrachloroethane was added over 8 minutes. After two hours reflux with continuous stirring, heating was discontinued and the mixture was allowed to cool to 25°C. The reaction mixture was transferred to a rotary evaporator with gentle heating at between 50 and 55°C. After 1 hour, when most of the volatiles had been removed, the reaction mixture was added to methanol (each 25 milliliters of solution was added to 0.75 liter of methanol) to precipitate the polymer using a Waring blender. The precipitated polymer was collected by filtration, washed with methanol, and air-dried to yield 13 grams of off-white powder. The polymer had about 1.5 CH_2Cl groups per repeat unit.

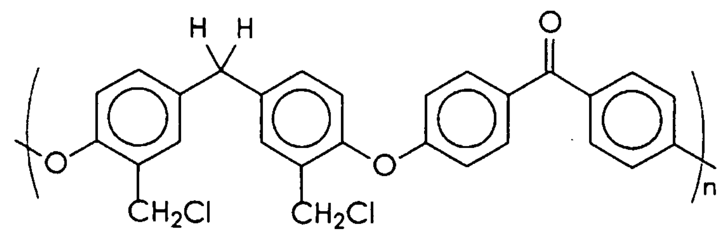
EXAMPLE III

A polymer of the formula



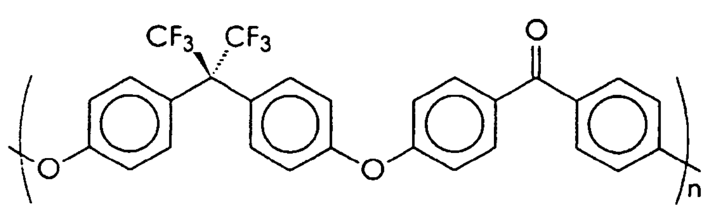
wherein n represents the number of repeating monomer units was prepared as follows. A 500 milliliter, 3-neck round-bottom flask equipped with a Dean-Stark (Barrett) trap, condenser, mechanical stirrer, argon inlet, and stopper was situated in a silicone oil bath. 4,4'-Dichlorobenzophenone (Aldrich 11,370, Aldrich Chemical Co., Milwaukee, WI, 16.32 grams, 0.065 mol), bis(4-hydroxyphenyl)methane (Aldrich, 14.02 grams, 0.07 mol), potassium carbonate (21.41 grams), anhydrous N,N-dimethylacetamide (100 milliliters), and toluene (100 milliliters) were added to the flask and heated to 175°C (oil bath temperature) while the volatile toluene component was collected and removed. After 48 hours of heating at 175°C with continuous stirring, the reaction mixture was filtered and added to methanol to precipitate the polymer, which was collected by filtration, washed with water, and then washed with methanol. The yield of vacuum dried product, poly(4-CPK-BPM), was 24 grams. The polymer dissolved on heating in N-methylpyrrolidinone, *N,N*-dimethylacetamide, and 1,1,2,2-tetrachloroethane. The polymer remained soluble after the solution had cooled to 25°C.

The resulting polymer poly(4-CPK-BPM) was subsequently chloromethylated as follows. A solution of chloromethyl methyl ether (6 mmol/milliliter) in methyl acetate was prepared by adding acetyl chloride (35.3 grams) to a mixture of dimethoxymethane (45 milliliters) and methanol (1.25 milliliters). The solution was diluted with 150 milliliters of 1,1,2,2-tetrachloroethane and then tin tetrachloride (0.3 milliliters) was added. After taking the mixture to reflux using an oil bath set at 110°C, a solution of poly(4-CPK-BPM) (10 grams) in 125 milliliters of 1,1,2,2-tetrachloroethane was added. Reflux was maintained for 2 hours and then 5 milliliters of methanol were added to quench the reaction. The reaction solution was added to 1 gallon of methanol using a Waring blender to precipitate the product, chloromethylated poly(4-CPK-BPM), which was collected by filtration and vacuum dried. The yield was 9.46 grams of poly(4-CPK-BPM) with 2 chloromethyl groups per polymer repeat unit. The polymer had the following structure:



EXAMPLE IV

A polymer of the formula



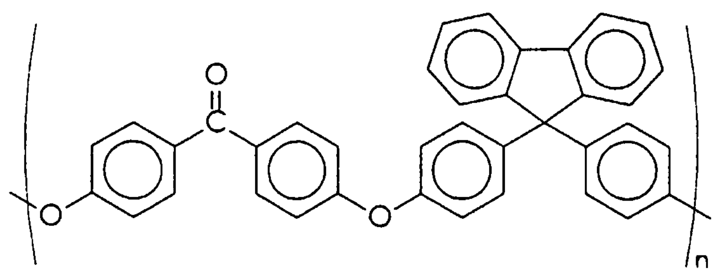
wherein n represents the number of repeating monomer units was prepared as follows. A 500 milliliter, 3-neck round-bottom flask equipped with a Dean-Stark (Barrett) trap, condenser, mechanical stirrer, argon inlet, and stopper was situated in a silicone oil bath. 4,4'-Dichlorobenzophenone (Aldrich 11,370, Aldrich Chemical Co., Milwaukee, WI, 16.32 grams, 0.065 mol), hexafluorobisphenol A (Aldrich, 23.52 grams, 0.07 mol), potassium carbonate (21.41 grams), an-

hydrous N,N-dimethylacetamide (100 milliliters), and toluene (100 milliliters) were added to the flask and heated to 175°C (oil bath temperature) while the volatile toluene component was collected and removed. After 48 hours of heating at 175°C with continuous stirring, the reaction mixture was filtered and added to methanol to precipitate the polymer, which was collected by filtration, washed with water, and then washed with methanol. The yield of vacuum dried product, poly(4-CPK-HFBPA), was 20 grams. The polymer was analyzed by gel permeation chromatography (gpc) (elution solvent was tetrahydrofuran) with the following results: M_n 1,975, M_{peak} 2,281, M_w 3,588, and M_{z+1} 8,918.

The polymer poly(4-CPK-HFBPA), prepared as above, is chloromethylated by the process described in Example III. It is believed that similar results will be obtained.

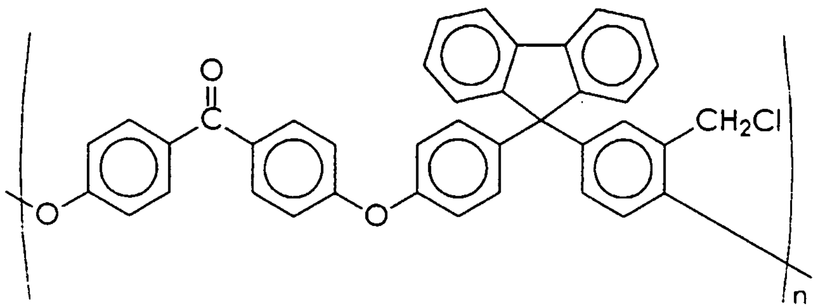
EXAMPLE V

A polymer of the formula



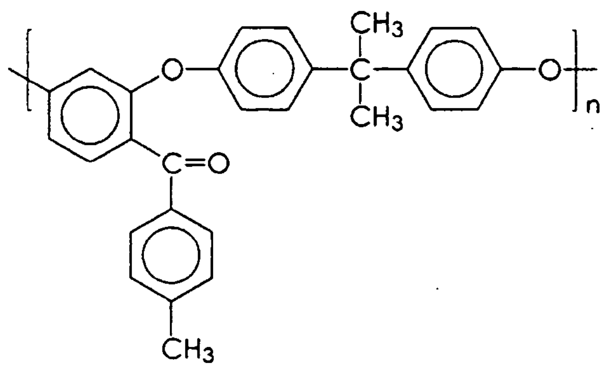
wherein n represents the number of repeating monomer units was prepared as follows. A 1-liter, 3-neck round-bottom flask equipped with a Dean-Stark (Barrett) trap, condenser, mechanical stirrer, argon inlet, and stopper was situated in a silicone oil bath. 4,4'-Dichlorobenzophenone (Aldrich Chemical Co., Milwaukee, WI, 50.02 grams, 0.1992 mol), 9,9'-bis(4-hydroxyphenyl)fluorenone (Ken Seika, Rumson, NJ, 75.04 grams, 0.2145 mol), potassium carbonate (65.56 grams), anhydrous N,N-dimethylacetamide (300 milliliters), and toluene (52 milliliters) were added to the flask and heated to 175°C (oil bath temperature) while the volatile toluene component was collected and removed. After 24 hours of heating at 175°C with continuous stirring, the reaction mixture was allowed to cool to 25°C. The reaction mixture was filtered and added to methanol to precipitate the polymer, which was collected by filtration, washed with water, and then washed with methanol. The yield of vacuum dried product, poly(4-CPK-FBP), was 60 grams.

The polymer poly(4-CPK-FBP), prepared as described above, was chloromethylated as follows. A solution of chloromethyl methyl ether (6 mmol/milliliter) in methyl acetate was prepared by adding acetyl chloride (38.8 grams) to a mixture of dimethoxymethane (45 milliliters) and methanol (1.25 milliliters). The solution was diluted with 100 milliliters of 1,1,2,2-tetrachloroethane and then tin tetrachloride (0.5 milliliters) was added in 50 milliliters of 1,1,2,2-tetrachloroethane. After taking the mixture to reflux using an oil bath set at 100°C, a solution of poly(4-CPK-FBP) (10 grams) in 125 milliliters of 1,1,2,2-tetrachloroethane was added. The reaction temperature was maintained at 100°C for 1 hour and then 5 milliliters of methanol were added to quench the reaction. The reaction solution was added to 1 gallon of methanol using a Waring blender to precipitate the product, chloromethylated poly(4-CPK-FBP), which was collected by filtration and vacuum dried. The yield was 9.5 grams of poly(4-CPK-FBP) with 1.5 chloromethyl groups per polymer repeat unit. When the reaction was carried out at 110°C (oil bath set temperature), the polymer gelled within 80 minutes. The polymer had the following structure:



EXAMPLE VI

A polymer of the formula

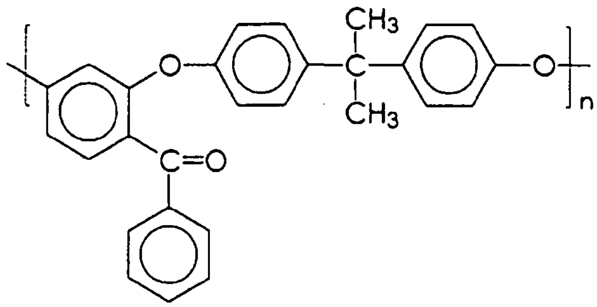


wherein n represents the number of repeating monomer units was prepared as follows. A 250 milliliter, 3-neck round-bottom flask equipped with a Dean-Stark (Barrett) trap, condenser, mechanical stirrer, argon inlet, and stopper was situated in a silicone oil bath. 4'-Methylbenzoyl-2,4-dichlorobenzene (0.0325 mol, 8.6125 grams, prepared as described in Example XIV), bis-phenol A (Aldrich 23,965-8, 0.035 mol, 7.99 grams), potassium carbonate (10.7 grams), anhydrous *N,N*-dimethylacetamide (60 milliliters), and toluene (60 milliliters, 49.1 grams) were added to the flask and heated to 175°C (oil bath temperature) while the volatile toluene component was collected and removed. After 24 hours of heating at 175°C with continuous stirring, the reaction product was filtered and the filtrate was added to methanol to precipitate the polymer. The wet polymer cake was isolated by filtration, washed with water, then washed with methanol, and thereafter vacuum dried. The polymer (7.70 grams, 48% yield) was analyzed by gel permeation chromatography (gpc) (elution solvent was tetrahydrofuran) with the following results: M_n 1,898, M_{peak} 2,154, M_w 2,470, M_z 3,220, and M_{z+1} 4,095.

A polymer having chloromethyl pendant groups thereon is prepared as follows. The polymer prepared as described above is chloromethylated by the process described in Example III. It is believed that similar results will be obtained.

EXAMPLE VII

A polymer of the formula

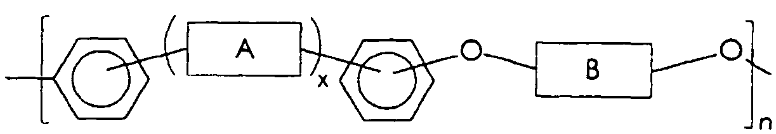


wherein n represents the number of repeating monomer units was prepared by repeating the process of Example XIX except that the 4'-methylbenzoyl-2,4-dichlorobenzene starting material was replaced with 8.16 grams (0.0325 mol) of benzoyl-2,4-dichlorobenzene, prepared as described in Example XV, and the oil bath was heated to 170°C for 24 hours.

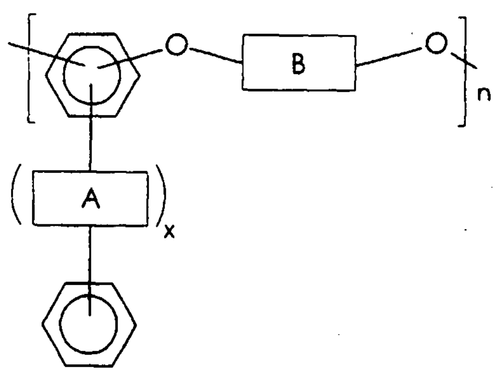
A polymer having chloromethyl pendant groups thereon is prepared as follows. The polymer prepared as described above is chloromethylated by the process described in Example III. It is believed that similar results will be obtained.

Claims

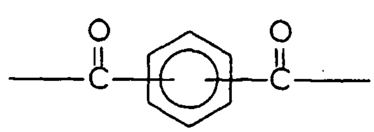
1. A process which comprises reacting a polymer of the formula

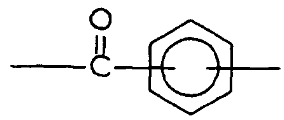


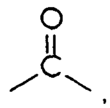
or

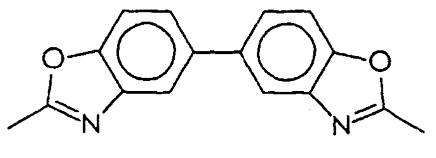


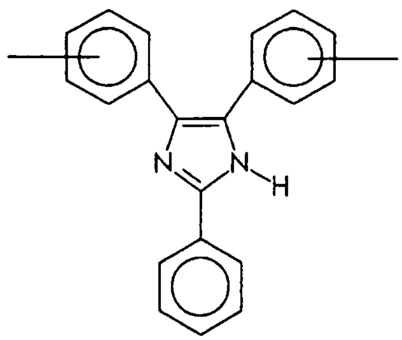
wherein x is an integer of 0 or 1, A is

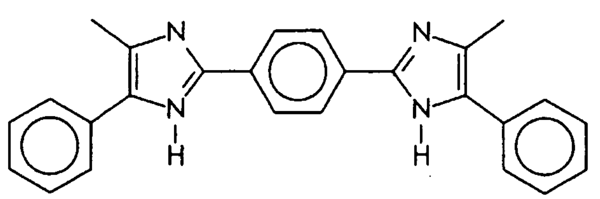








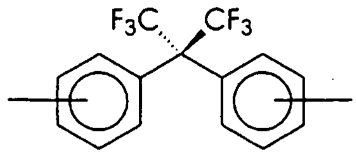




-O-,

$-C(CH_3)_2-$,

or mixtures thereof, B is



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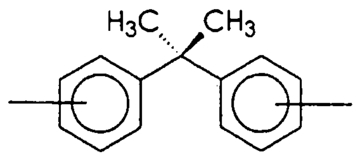

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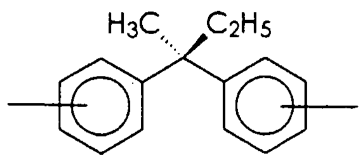

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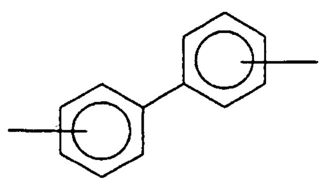

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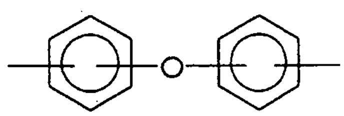

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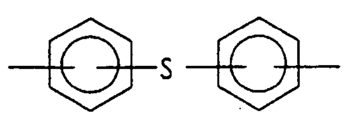

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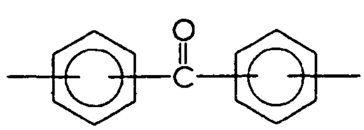

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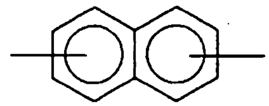

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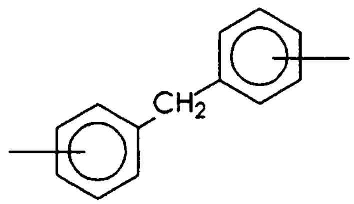

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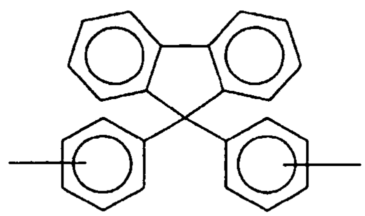

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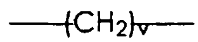

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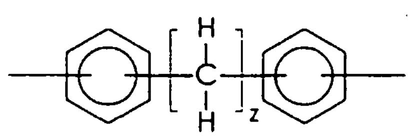
wherein v is an integer of from 1 to about 20,



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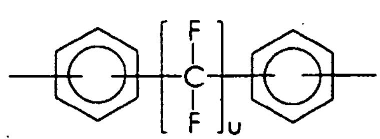
wherein z is an integer of from 2 to about 20,



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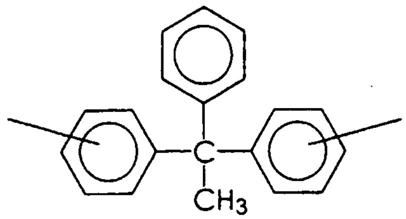
wherein u is an integer of from 1 to about 20,



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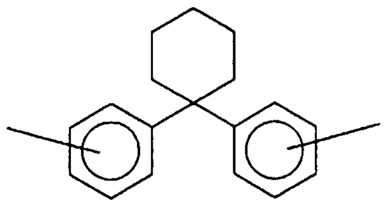

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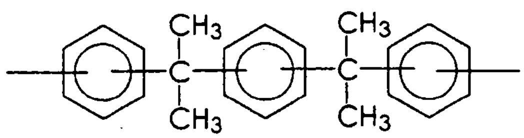

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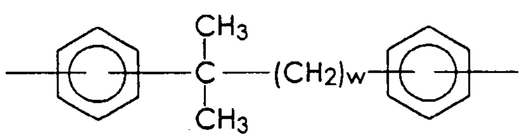

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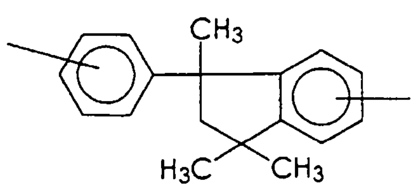
wherein w is an integer of from 1 to about 20,



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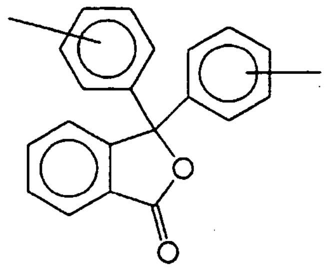
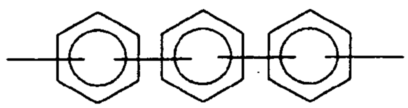
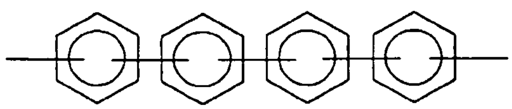
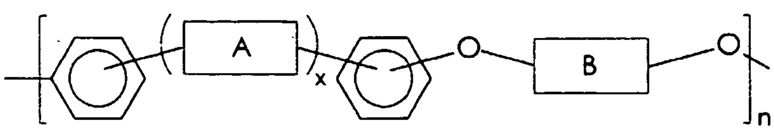






or mixtures thereof, and n is an integer representing the number of repeating monomer units, with an acetyl halide and dimethoxymethane in the presence of a halogen-containing Lewis acid catalyst and methanol, thereby forming a haloalkylated polymer.

2. A process which comprises the steps of: (a) reacting a polymer of the formula



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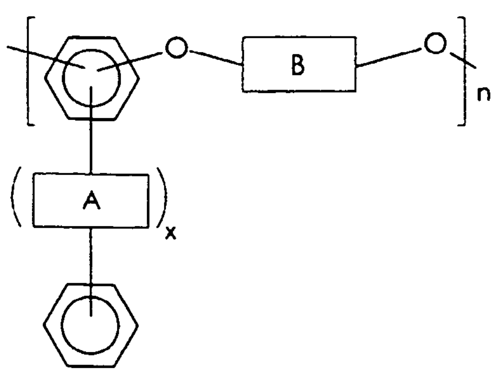
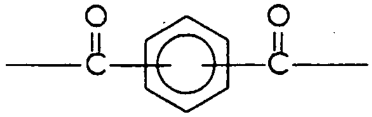


wherein x is an integer of 0 or 1, A is



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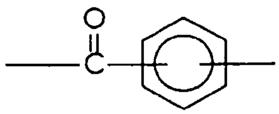

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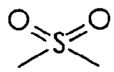

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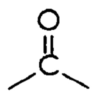

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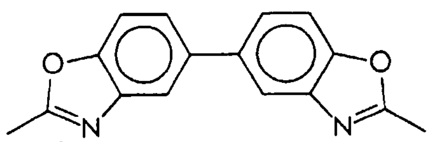

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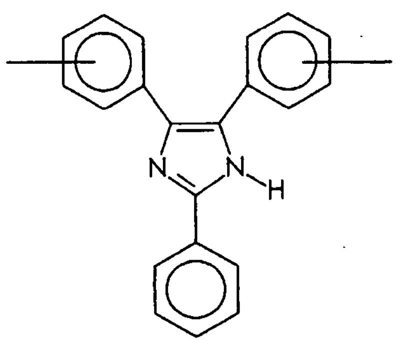

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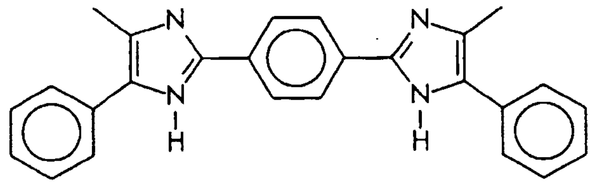
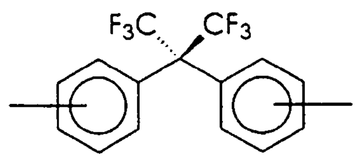


,

-O-,

$-C(CH_3)_2-$,

or mixtures thereof, B is



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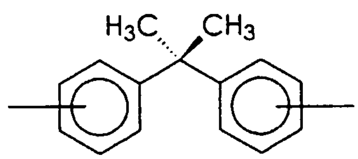

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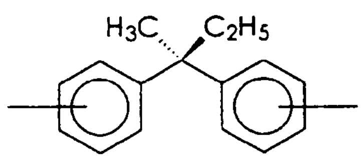

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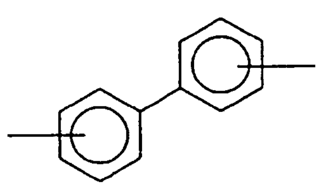

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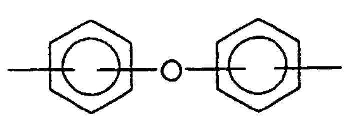

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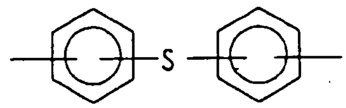

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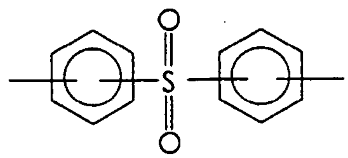

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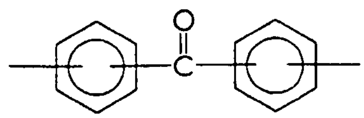

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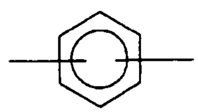

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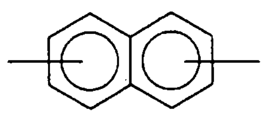

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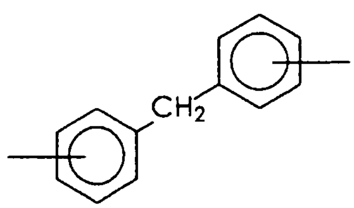
CH2

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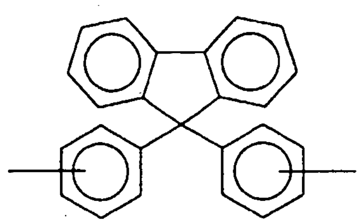
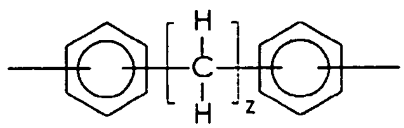


,

$$-\!\!\left(CH_2\right)_v\!\!-$$,

wherein v is an integer of from 1 to about 20,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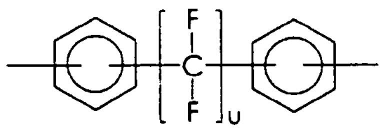
wherein z is an integer of from 2 to about 20,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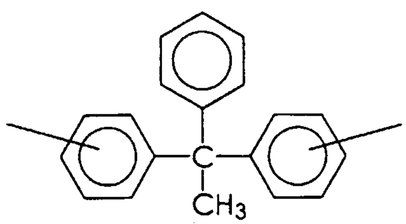
wherein u is an integer of from 1 to about 20,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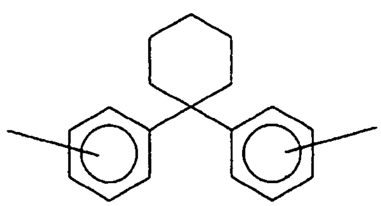
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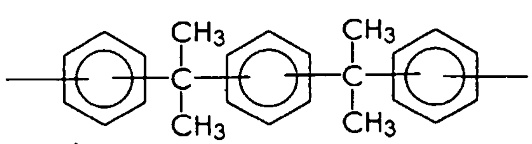
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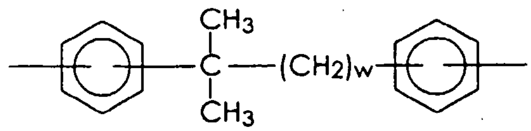
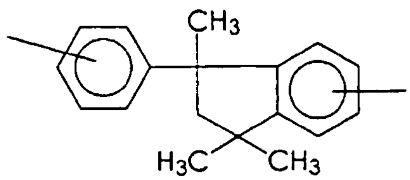


wherein w is an integer of from 1 to about 20,



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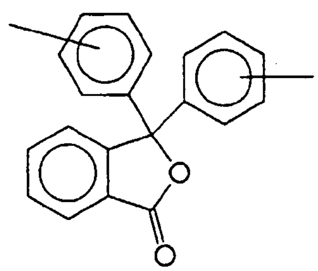

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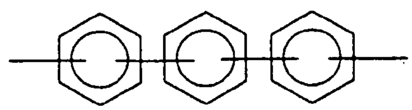

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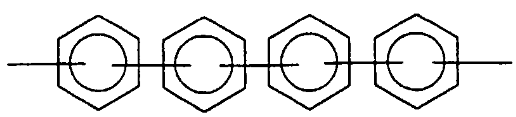


,

or mixtures thereof, and n is an integer representing the number of repeating monomer units, with an acetyl halide and dimethoxymethane in the presence of a halogen-containing Lewis acid catalyst and methanol, thereby forming a haloalkylated polymer; and (b) converting at least some of the haloalkyl groups to photosensitivity-imparting groups which enable crosslinking or chain extension of the polymer upon exposure to actinic radiation, thereby forming a photopatternable polymer.

3. A process according to claim 2 further comprising the step of causing the polymer to become crosslinked or chain extended through the photosensitivity-imparting groups.

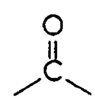
4. A process according to claim 3 wherein crosslinking or chain extension is effected by heating the polymer to a temperature sufficient to enable the photosensitivity-imparting groups to form crosslinks or chain extensions in the polymer, or by exposing the polymer to actinic radiation such that the polymer in exposed areas becomes

crosslinked or chain extended.

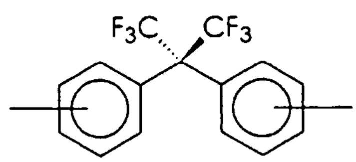
5. A process according to claim 1 wherein the haloalkyl groups on the polymer are halomethyl groups, and further comprising the step of causing the polymer to become crosslinked or chain extended through the halomethyl groups by heating the polymer to a temperature sufficient to enable the halomethyl groups to form crosslinks or chain extensions in the polymer.

6. A process according to claim 5 wherein prior to crosslinking or chain extension the polymer is admixed with a solvent to form a solution containing from about 30 to about 60 percent by weight of the polymer, followed by filtration of the solution through a 2 micron nylon filter cloth under positive pressure.

7. A process according to any of claims 1 to 6 wherein A is



and B is



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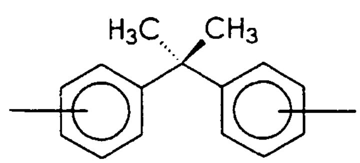

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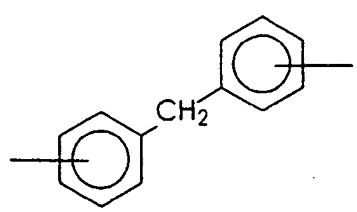

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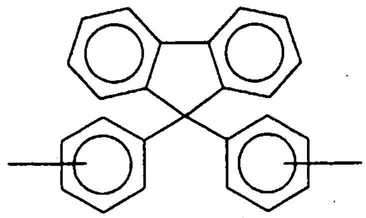

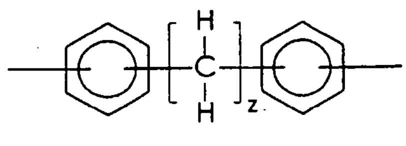

wherein z is an integer of from 2 to about 20, or a mixture thereof.

8. A process according to any of claims 1 to 7 wherein the polymer has end groups derived from the "A" groups of the polymer.

9. A process according to any of claims 1 to 7 wherein the polymer has end groups derived from the "B" groups of the polymer.

10. A process for forming a thermal ink jet printhead comprising the steps of:

(a) depositing a layer (18) comprising a polymer obtainable by the process of any of claims 1 to 9 onto a lower substrate (28) in which one surface thereof has an array of heating elements (34) and addressing electrodes (33) having terminal ends (32) formed thereon;
(b) exposing the layer (18) to actinic radiation in an imagewise pattern such that the polymer in exposed areas becomes crosslinked or chain extended and the polymer in unexposed areas does not become crosslinked or chain extended, wherein the unexposed areas correspond to areas of the lower substrate (28) having thereon the heating elements (34) and the terminal ends (32) of the addressing electrodes (33);
(c) removing the polymer from the unexposed areas, thereby forming recesses in the layer (18), said recesses exposing the heating elements (34) and the terminal ends (32) of the addressing electrodes (33);
(d) providing an upper substrate (31) with a set of parallel grooves (20) for subsequent use as ink channels and a recess (24) for subsequent use as a manifold, the grooves (20) being open at one end for serving as droplet emitting nozzles; and
(e) aligning, mating, and bonding the upper (31) and lower (28) substrates together to form a printhead with the grooves (20) in the upper substrate (31) being aligned with the heating elements in the lower substrate (28) to form droplet emitting nozzles, thereby forming a thermal ink jet printhead.

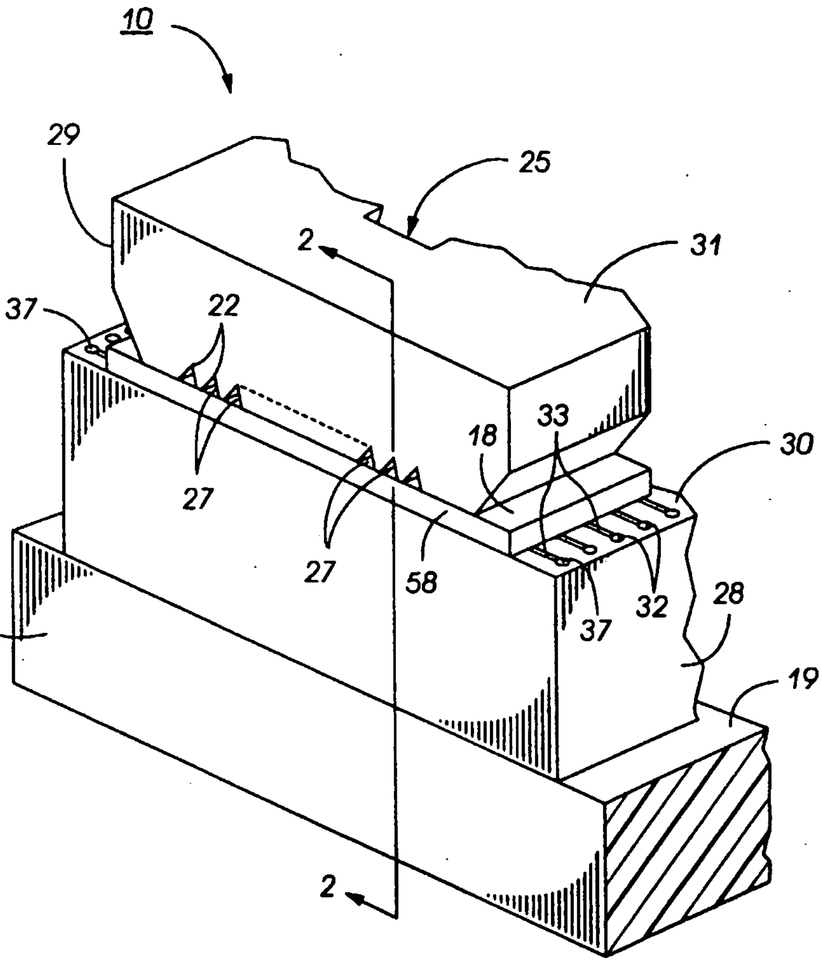

FIG. 1

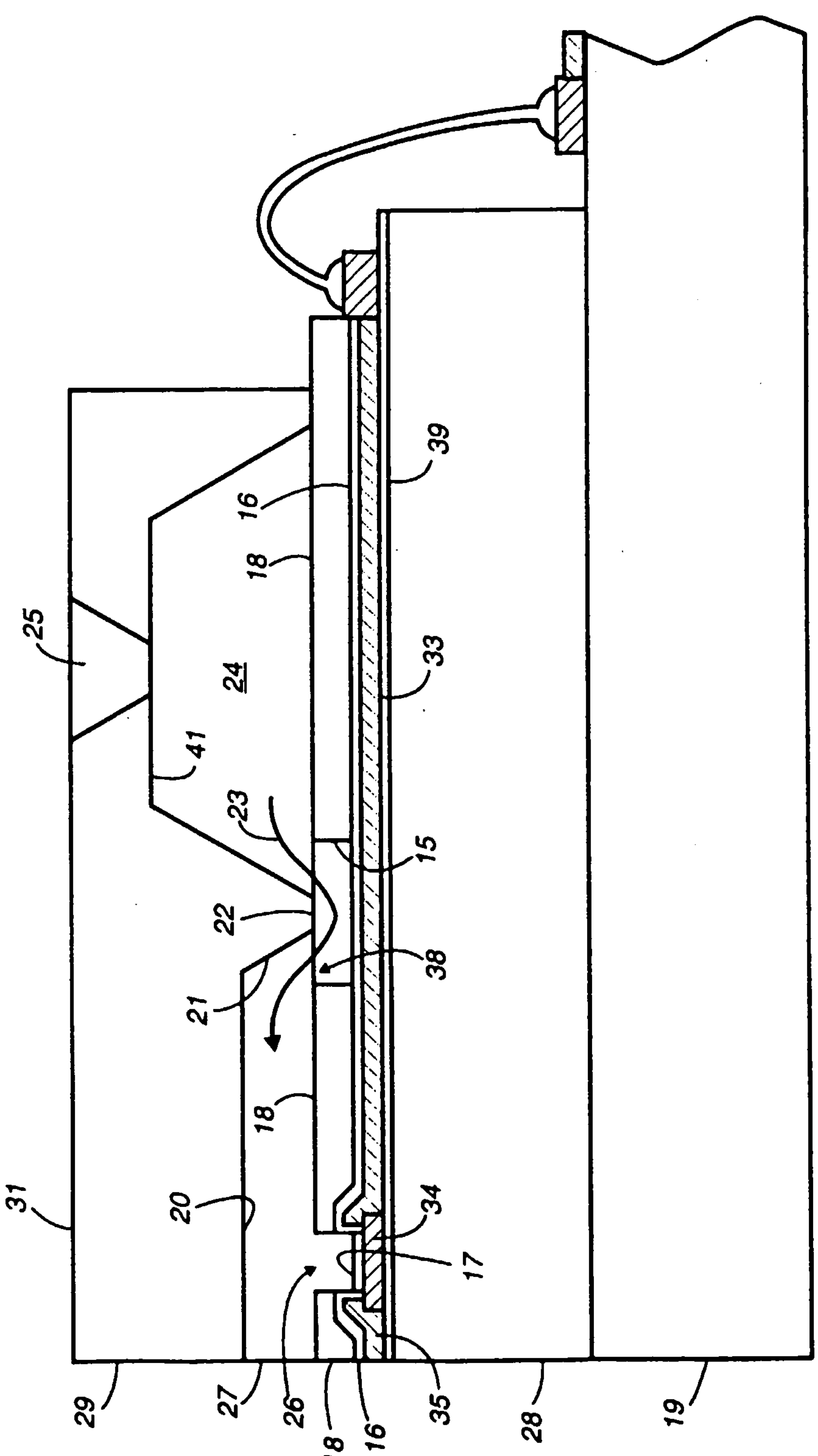
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FIG. 2

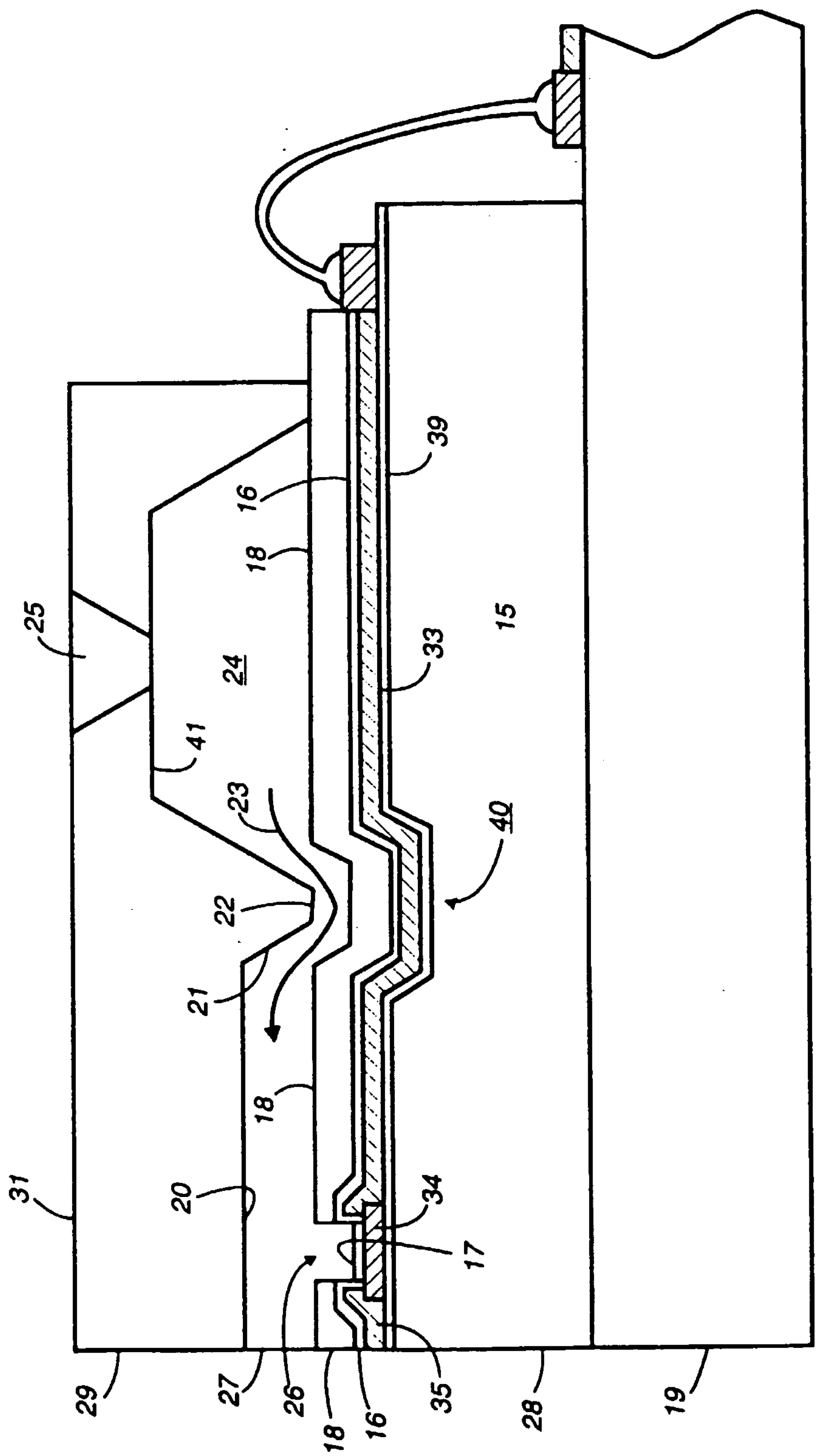

FIG. 3

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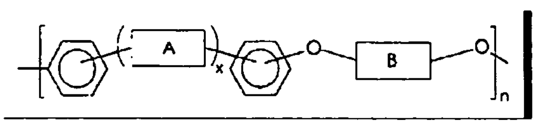
(71) Applicant: XEROX CORPORATION
Rochester, New York 14644 (US)

(72) Inventors:
, Fuller, Timothy J.
Pittsford, NY 14534-4023 (US)
, Narang, Ram S.
Fairport, NY 14450 (US)
, Smith, Thomas W.
Penfield, NY 14526 (US)
, Luca, David J.
Rochester, NY 14609 (US)
, Crandall, Raymond K.
Pittsford, NY 14534 (US)

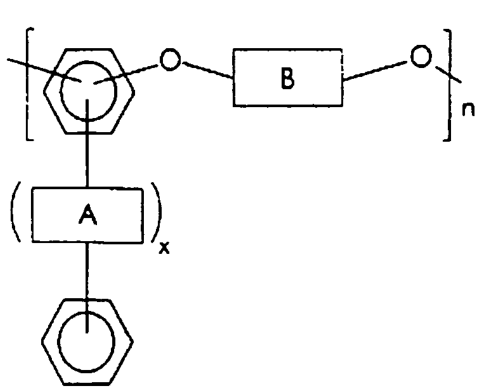
(74) Representative:
Grünecker, Kinkeldey,
Stockmair & Schwanhäusser
Anwaltssozietät
Maximilianstrasse 58
80538 München (DE)

(54) **Process for haloalkylation of high performance polymers**

(57) Disclosed is a process which comprises reacting a polymer of the general formula



or



wherein x is an integer of 0 or 1, A and B are specified groups, and n is an integer representing the number of repeating monomer units, with an acetyl halide and dimethoxymethane in the presence of a halogen-containing Lewis acid catalyst and methanol, thereby forming a haloalkylated polymer. In a specific embodiment, the haloalkylated polymer is then reacted further to replace at least some of the haloalkyl groups with photosensitivity-imparting groups. Also disclosed is a process for preparing a thermal ink jet printhead with the aforementioned polymer.

EP 0 826 700 A3

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EUROPEAN SEARCH REPORT

Application Number
EP 97 30 6206

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	30 October 2000	Permentier, W

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EUROPEAN SEARCH REPORT

Application Number
EP 97 30 6206

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